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Investigation of phase composition of ilmenites and influence of this parameter on thermokinetics of reaction with sulphuric acid

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Abstract Ilmenite is a valuable source of titanium and is applied as the main raw material in the technology of titanium white pigment production. Ilmenite is found in many places in the earth, and its elemental as well as phase compositions very strongly depend on the place of origin. Deposits located in Australia, China, India, and Norway in Europe are well known places where ilmenites are exploited industrially. Main phases that were identified in these ilmenites are ilmenite $FeTiO_3$, hematite Fe_2O_3, geikielite $MgTiO_3$ and pseudorutile $Fe_2Ti_3O_9$. Enstatite $MgSiO_3$, $MnTiO_3$, and kleberite (determined also as hydroxylian pseudorutile with approximate formula $FeTi_3O_6(OH)_3$) are minor phases present in ilmenites. Calorimetric investigations of reactions of these ilmenites with sulphuric acid in standard conditions demonstrated significant differences in the shape of temperature and thermal power curves. On the basis of these investigations, it can be concluded that the shape of the thermal power curve is different for each of ilmenite and can be treated as a fingerprint of their phase composite.

Keywords Ilmenite · Phase composition · Thermokinetics · Calorimetric investigations

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Introduction

Ilmenite is a universally observed mineral on the earth, and it is a main source of titanium, and its compounds are used extensively in the industry. The industrial exploitation of ilmenite deposit is feasible when given deposit contains appropriate concentration of the raw material. Composition of the titanium raw material strongly depends on the place of its origin and is an important factor that must be taken into consideration. Main differences are observed in the contents of trace and accompanying elements. Ilmenite is extracted from rock deposits, alluvial deposits and also from sedimentary rocks formed as a result of atmospheric erosion. Almost one half of the ilmenite production comes from seaside and riverside sands. Considerable part of this type of ilmenite is produced from deposits in Australia [1].

Ilmenites differ not only in elemental composition, but also in phase composition. Ilmenite is one of the main raw materials for the titanium dioxide production using sulphuric acid technology, and one of the first stages of the production is the reaction of the titanium raw material with the sulphuric acid. Elemental and phase compositions of ilmenite have an influence on the way of processing. Thermokinetics of this reaction play very important roles. Efficiency, quality, as well as the safety of the process depend on elemental and phase compositions of ilmenite.

Phase composition of ilmenites is very important not only in the sulphuric technology but also in different technologies using ilmenite as the raw material [2, 3].

Investigation of the reaction kinetics is very important especially in processes with the possibility of danger of thermal explosion [4, 5]. The reaction of the sulphuric acid with titanium raw materials is posing exactly such a kind of danger of the thermal explosion, and therefore the

knowledge of phase composition as one of parameters of the process is very important.

Influence of phase composition of titanium raw material on the reaction kinetics with sulphuric acid is visible especially in the case of titanium slag. Phase composition of this titanium raw material in comparison with ilmenite is completely different as well as conditions of reaction with sulphuric acid [6].

In the present article, we have performed a detailed analysis of the elemental and phase compositions of ilmenites from four places and discussed their properties in relation to the temperature and thermal power curves obtained during their reactions with sulphuric acid.

Experimental

Elemental and phase compositions of titanium raw materials play very significant roles, because of their influences on thermokinetics of the reaction with sulphuric acid as mentioned above. Analysis of composition of titanium raw materials has been a subject of several earlier articles [1, 7, 8]. The X-ray fluorescence (XRF) and the X-ray diffraction (XRD) are most often applied for this analysis. In the present study, for elemental composition of titanium raw materials, the spectrometer XRF Philips PW 1480 was used. The spectrometer was equipped with the X-ray tube with the Rh type anode. The quantitative analysis was realized by applying the standard procedure of calibration. Channels in analyser were calibrated with use of universal standards (of the Omega firm).

Analysis of the phase composition of samples was performed by diffractometer Philips PW 1710, equipped with the X-ray tube with Cu anode (voltage 40 kV and current 35 mA). Samples for analysis were prepared in the form of powders and placed on special holder.

The X-ray absorption spectra at the K-edges of Fe, V, Mn, Cr, and Ti were measured at A1 station at HASYLAB, Hamburg and at the K-edges of Mg, Al, and Si at BESSY II synchrotron, station UE52-PGM.

Thermal analysis method is one of the important research techniques used for verifying the phase composition of titanium raw materials. The thermal transformations of ilmenite were investigated applying thermogravimeter MOM 1500C in the range of temperatures from 20 to 1,000 °C in the static air atmosphere. The sample of ilmenite before the measurement was grounded in a ball mill, and then dried to the constant mass at 105 °C. The sample's mass taken for measurements was 100 mg. The shape of the crucible and the sample mass were selected to limit the influence of the diffusion on the kinetics of the process. A number of measurements were carried out at different rates of heating. It was found that influence of heating rate on the mass changes of the sample is negligible. The results of the process of sample heating can be used also for estimation of iron(II) contents in ilmenites [9].

Thermokinetic investigations of the reaction of the sulphuric acid with samples of ilmenites were realized in the calorimeter described in the earlier article [10]. Reaction of the sulphuric acid with ilmenite is strongly exothermic. During the process, apart from heat, vapours and gases are also emitted, which cause danger of the explosion. Therefore, the applied calorimeter has to be appropriately adapted for conditions of reaction. The calorimetric vessel has to be resistant towards strongly corroding environment and equipped with the safety valve.

Results and discussion

The methods presented were applied for characterization of ilmenites from the deposits in southern Norway, Australia, India and China. The ilmenites mentioned have been the subject of many previous studies [11–13].

In Figure 1, the results of XRF estimation of the elements content in ilmenites expressed in the form of the main oxides content are presented.

The lowest content of titanium dioxide was found in Norwegian ilmenite. Maximum content of the titanium dioxide was found in Australian ilmenite (at the level of 55%). Contents of the iron oxide(II) were changing from 38% for Australian, 41% for China and about 46% for Norwegian and India. Besides differences in titanium and iron contents, significant differences appear in the concentration of accompanying elements, for example, magnesium MgO from 0.18 to 5.1%, or silicon SiO_2 from 1.1 to 3.5%.

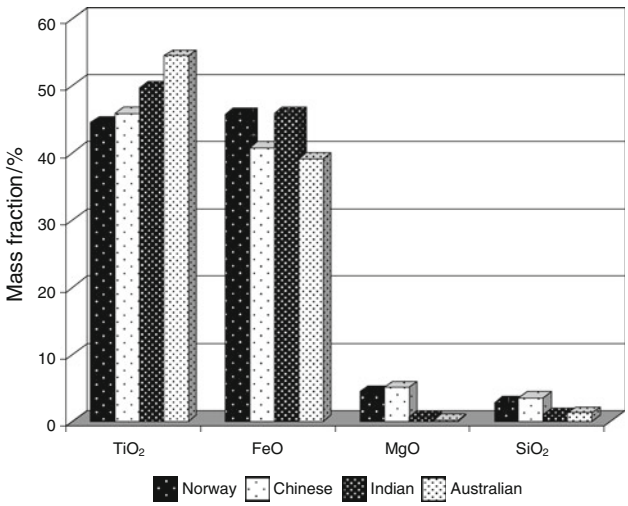

Fig. 1 The composition of ilmenites from XRF measurements expressed in the form of oxides

Investigation of the phase composition of ilmenites is more complicated and requires application of different analytical techniques. Results of investigation by means of XRD are presented in Fig. 2. The obtained diffractograms show major similarity, and practically all peaks are located at the similar angles for all the samples. Some differences can be noticed between the given main peaks' intensities, and some additional peaks appear with very small intensities. These small peaks are indicative of the presence of different minority phases. As a result of diffractogram analysis, it was found that in all cases, a dominating phase was ilmenite ($FeTiO_3$). The presence of the hematite (Fe_2O_3) and enstatite ($MgSiO_3$) was also detected in all samples.

Standard investigation by X-ray diffraction does not provide information about the relative abundance of the identified phases because of large similarities between phase structures. In order to confirm the presence of the identified phases and estimate their abundance, we can apply other methods, such as X-ray absorption near edge structure (XANES) measurements [14], or thermogravimetric (TG) measurements, as well as the method based on balancing components estimated in the XRF. These methods can be used also for quantitative determination of main and minor phases in ilmenite.

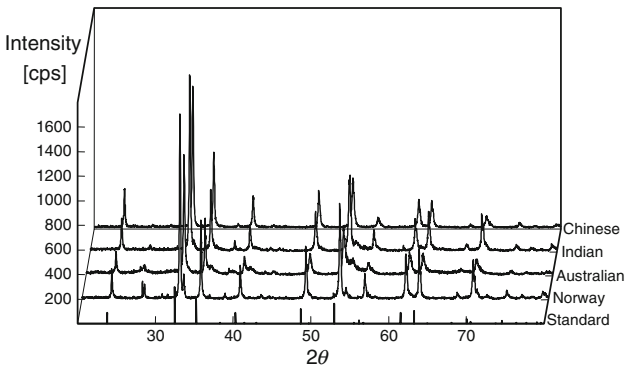

Fig. 2 Diffractograms of ilmenites

It should be mentioned that laboratory techniques such as XRF, XRD or thermogravimetry are relatively easy to apply in contrast to the XANES method which requires the access to the synchrotron because of the requirements for high X-ray intensity in the wide energy range. However, XANES method allows identification of the trace elements' phases, which is impossible by other methods [15]. Applying Linear Component Analysis (LCA) of the XANES spectra, one can get quantitative information about relative abundance of compounds in the investigated material [15]. Using LCA, one can identify the major phases of Ti and Fe as well as the phases of minority elements (Mg, Mn, Cr, Si and Al). The results of identification of the phases by XANES are presented in the Table 1.

The phases identified by XANES were applied next to the phase analysing balancing contents of elements estimated in the XRF (or single particle electron probe microanalysis SPEPMA), and as a starting point in XRD analysis. The details of such analysis for Norwegian ilmenite have been presented in Ref. [7]. The results of the analysis performed for all the investigated samples are presented in Table 2. The results from XRD and SPEPMA techniques considerably differ particularly for the main phases of Ti and Fe.

The content of ilmenite resulting from XRD is of the order of 90%, and other identified phases are of the orders of a few percent. In the case of SPEPMA analysis, the content of ilmenite phase depends on the location of the deposit, and it is about 50% in Australia and exceeds 60%

Table 1 The results by the XANES method of the relative abundances of phases for elements identified in ilmenities originated from Norway, Australia, China and India

Element	Chemical compound	Norwegian ilmenites/%	Australian ilmenites/%	Chinese ilmenites/%	Indian ilmenites/%
Fe	$FeTiO_3$	86.8	72.4	80.3	84.9
	Fe_2O_3	13.2	27.6	19.7	15.1
Mg	$MgTiO_3$	57.5	~100		
	$MgSiO_3$	30.3		~100	
	$MgO/Mg(OH)_2$	12.2			~100
Ti	$FeTiO_3$	99	96.7	~100	~100
	$MgTiO_3$	1	3.3		
Si	$MgSiO_3$	~100		~100	~100
Mn	$MnTiO_3$	~100	~100	~100	~100
Al	Al_2O_3	~100		~100	
	$Al(OH)_3$				~100
Cr	Cr_2O_3	~100	~100	~100	~100

For each element, the phases were normalized to 100%

Table 2 The phase analysis of the investigated ilmenities by XRD and single particle electron probe microanalysis (SPEPMA)

Chemical compound	Contents/%							
	Norwegian ilmenites		Australian ilmenites		Chinese ilmenites		Indian ilmenites	
	SPEPMA	XRD	SPEPMA	XRD	SPEPMA	XRPD	SPEPMA	XRD
$FeTiO_3$	63.5	86.7	49.8	93.7	59.8	95.4	–	95.2
Fe_2O_3	5.1	2.1	5.8	4.8	6.4	–	–	1.8
$Fe_2Ti_3O_9$	–	–	33.2	1.2	13.3	1.3	–	2.7
Fe_2TiO_5	–	–	–	–	–	2	–	–
$MgTiO_3$	13.4	3.2	2.6	–	–	–	–	–
$MgSiO_3$	8.3	8.1	–	–	–	–	–	–
$MgO/Mg(OH)_2$	5.1	–	–	–	5.9	–	–	–
SiO_2	3.5	–	2.6	–	7.2	1.3	–	–
TiO_2	–	–	–	0.3	–	–	–	0.3
Al_2O_3	1.1	–	2.6	–	5.6	–	–	–
Cr_2O_3	–	–	–	–	0.5	–	–	–
V_2O_3	–	–	–	–	0.2	–	–	–
$MnTiO_3$	–	–	2.6	–	1.1	–	–	–

The content of all compounds was normalized to 100%

in Norway. These differences indicated about the possibility of the formation of the amorphous phases which are not detected by XRD. Moreover, such elements as Mg and Mn can substitute Fe in ilmenites, which is not detected in XRD but resulted only in the broadening of the diffraction peaks. The minority phases of Si, Al, Cr or V identified by SPEPMA are of the order of magnitudes several percent, and therefore are not distinguishable in XRD with the background of majority phase.

The comparison of the quantitative contents of ilmenite and hematite phases (based on the assumption that iron is found only in these two structures) in the case of Norwegian ilmenite resulting from all the applied methods is presented in Fig. 3. The presented results indicate that all methods are providing very similar results except that of the Rietveld method. This confirms that in the phase of ilmenite, the substitution of different elements occurred at the site of Fe. In the case of Norwegian ilmenite, the $MgTiO_3$ phase is the result of such a substitution. The other part of magnesium is observed in the phase of $MgSiO_3$ [15], which is confirmed by diffraction analysis.

In the case of other ilmenites, magnesium is most often found in a form of only one phase. For example in Australian ilmenite, magnesium appears only in the phase $MgTiO_3$; however, in the case of Indian ilmenite, magnesium is visible in the phase of $MgSiO_3$ (see Table 1).

In Fig. 4, results of the thermogravimetric measurement for the sample of Norwegian and Chinese ilmenite are

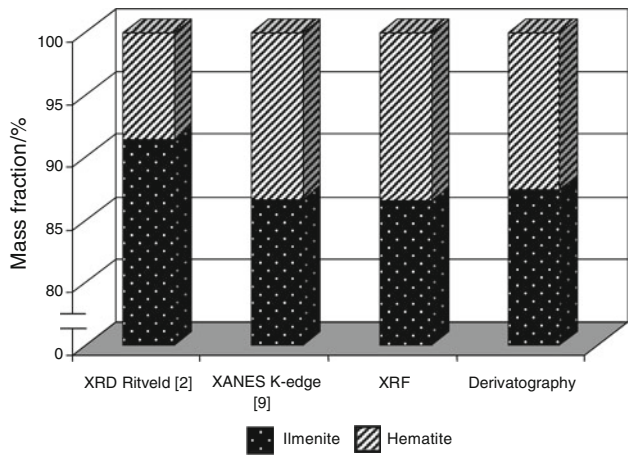

Fig. 3 The results of measurements of the content of ilmenite and hematite phases (at the assumption that iron is found only in these two structures) with different methods in the case of Norwegian ilmenite

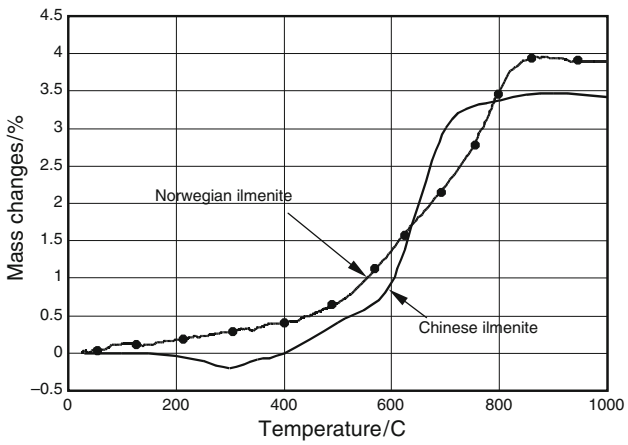

Fig. 4 The mass changes in the processes of heating of samples of Norwegian and Chinese ilmenites

presented. It can be noticed that, together with temperature rise, an increase in mass of the sample follows at first slowly, and after exceeding temperature of 500 °C much faster, until temperature reaches 800 °C. The mass increase stops at above 800 °C, and practically in the range of temperature from 850 to 1,000 °C mass of the sample did not change.

The performed analysis indicates that, in the range of temperatures from 500 to 800 °C, the phase of ilmenite vanishes, and at the same time the phase of hematite starts growing up accompanied by the major increase in the mass of the sample.

The mass changes in the process of heating (TG curve) for Chinese ilmenite are different in shape in comparison with Norwegian ilmenite (Fig. 4). In the initial period of Chinese ilmenite heating, a small decrease of mass in the range of temperatures from 200 to 300 °C is observed. Above this temperature, an opposite process is observed, i.e. an increase of the mass of the sample follows, up to the temperature of 800 °C. The mass changes in the initial period of heating and XRD measurements indicate the possibility of the presence of the hydroxylian pseudorutile (kleberite) with an approximate formula of $FeTi_3O_6(OH)_3$. This compound in Chinese ilmenite appears in small quantity. An estimated content of it is about 1%.

The main phases that were identified in Chinese ilmenite are the same as in the Norwegian ilmenite: ilmenite ($FeTiO_3$), hematite (Fe_2O_3) and $MgTiO_3$. Nevertheless, in Chinese ilmenite, also additional phases such as $CaSiO_3$ (2%) and $MnTiO_3$ (1%) were found.

Results of investigation of the mass changes in the process of heating for Indian ilmenite are similar to Chinese ilmenite; however, small differences are observed, mainly in initial parts of the curve as can be noticed in Fig. 5. In the initial period of heating to the temperature of 600 °C, the sample mass change is very small. The main transformation occurred in the range of temperatures from 600 to 800 °C.

Estimated contents of iron(II) and iron(III) on the basis of diffractogram and TG curve shows that the iron(III) is not only present in hematite but also in pseudorutile $Fe_2Ti_3O_9$. Remaining major component determined in Indian ilmenite was ilmenite ($FeTiO_3$).

Similarly, as in Chinese ilmenite, a decrease of the mass in the range of temperatures from 200 to 400 °C was observed in Australian ilmenite (Fig. 5) and similarly, as in previous ilmenites, mass increase is mainly observed for Australian ilmenite in the range of temperatures from 600 to 800 °C. In the same way as in the case of Chinese ilmenite, the mass decrease in the initial step of heating can be attributed to the presence of kleberite ($FeTi_3O_6(OH)_3$). Phases obtained as a result of the transformation in higher temperatures are the same as in the case of previous ilmenites.

Contents of iron(II) in Australian ilmenite are considerably lower than in the case of remaining ilmenites. This indicates on the presence of pseudorutile ($Fe_2Ti_3O_9$) in higher amount than in other ilmenites. The phase compositions for all the investigated ilmenites estimated by the method based on balancing components in the XRF are presented on Fig. 6.

The main phases identified in the investigated ilmenites were the following: ilmenite ($FeTiO_3$), hematite (Fe_2O_3), geikielite ($MgTiO_3$), pseudorutile ($Fe_2Ti_3O_9$) and enstatite ($MgSiO_3$) and in a small quantities as kleberite ($FeTi_3O_6(OH)_3$), $MnTiO_3$ and $CaSiO_3$. From the results presented, it follows that the highest content of ilmenite phase is in Norwegian ilmenite. The Chinese and Indian ilmenites contain smaller amount of ilmenite phase than Norwegian one. The lowest content of ilmenite phase was detected in Australian ilmenite, but in this ilmenite, on the contrary, the higher content of the pseudorutile phase was observed. In Chinese and Norwegian ilmenites, the pseudorutile phase was not detected but significant content of hematite and geikielite were present. In the case of Indian and Australian ilmenites, considerably

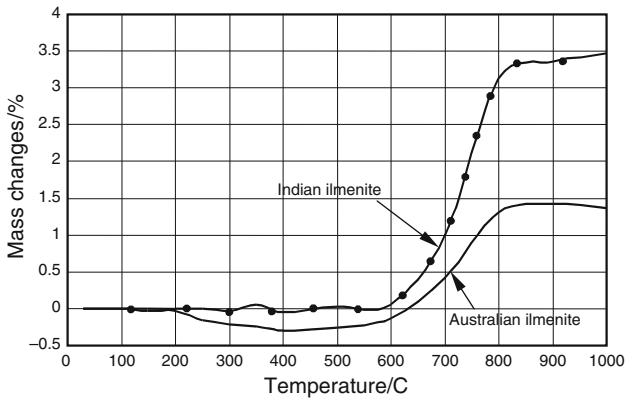

Fig. 5 The mass changes in the processes of heating of samples of Indian and Australian ilmenites

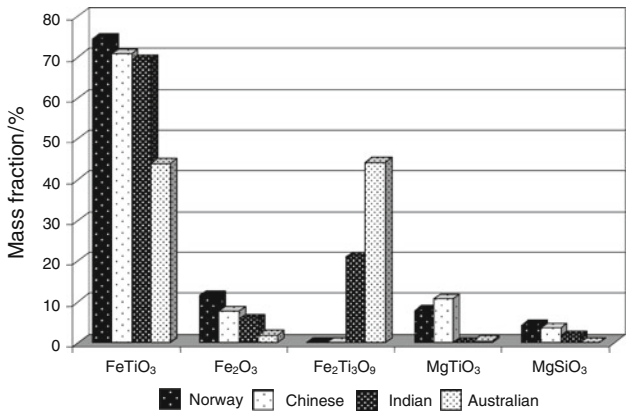

Fig. 6 Estimated phase compositions of samples of ilmenites by the method based on balancing results from XRF

smaller contents of hematite and lack of geikielite was observed.

The phase composition of ilmenites has its influence on thermokinetics of reaction with the sulphuric acid. In order to compare thermokinetics of ilmenites reaction with sulphuric acid, it is very important to determine initial conditions of this reaction. The optimal conditions (initial temperature of the reaction, particles size of the raw material and the initial concentration of the sulphuric acid) were determined for Norwegian ilmenite, and in these conditions, the reactions of other ilmenites were investigated. The influence of these parameters on thermokinetics of titanium raw materials' reaction with the sulphuric acid was described elsewhere [16, 17].

As a result of thermokinetic investigation, the temperature and thermal power curves were obtained (Figs. 7, 8). The presented results of the thermal power and the temperature changes in the reaction of ilmenites with sulphuric acid show significant differences. The maximum temperatures of reactionary mixture were obtained in the case of Norwegian (164 °C) and Chinese (155 °C) ilmenites, although, both curves differ in the shape. Main differences between these ilmenites are in the composition of accompanying phases and content of elements. Therefore, these accompanying components influence on the kinetics as well as the efficiency of the reaction. An exception here is the phase of enstatite ($MgSiO_3$), because as was found, this compound did not react with sulphuric acid [18]. In Fig. 7 also, a considerable difference is observed in the shape of curves of temperature changes for Indian and Australian ilmenites in comparison with Norwegian ilmenite. The main difference in phase composition among these ilmenites was the presence of the pseudorutile phase in Indian and Australian ilmenites.

Thermal power curves obtained in the reaction with samples of ilmenites are presented in Fig. 8. The presented results show large differences between the curves for Norwegian and other ilmenites. In the case of Norwegian ilmenite, after initiating the reaction, in contrast to the other ilmenites, the second maximum of thermal power is visible. In the case of remaining ilmenites, the maximum of the thermal power is related only with the moment of initiation of the reaction. Differences between curves show that the kinetics and the efficiency of the reaction influence contents in not only major but also minor phases.

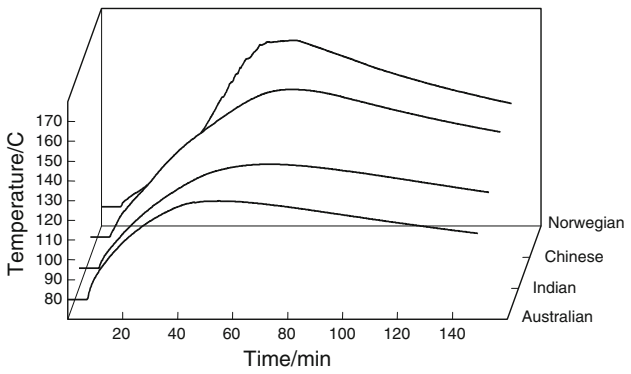

Fig. 7 The temperature changes in the reaction of ilmenites with sulphuric acid

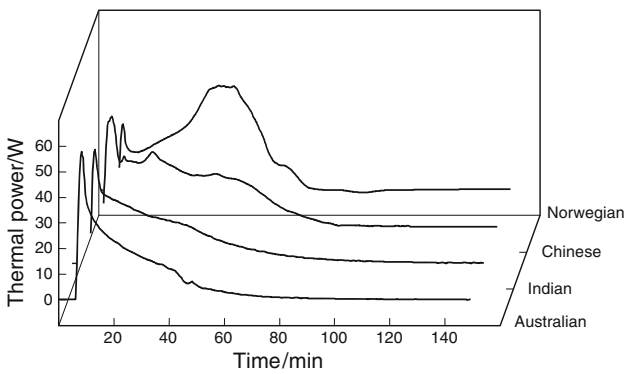

Fig. 8 The thermal power changes in the reaction of ilmenites with sulphuric acid

Conclusions

The performed investigations show that XANES and SPEPMA are very helpful methods for the determination of ilmenites phase composition. These methods allowed determining not only the main phases but also minority ones, based on accompanying elements, which is practically impossible to be determined by standard XRD and XRF methods.

Differences between the results provided by XANES and SPEPMA methods and those provided by remaining methods based on XRF measurements are due to the nonhomogeneity of the raw material and amount of the sample used in studies. In the case of the SPEPMA or XANES methods, the mass of the sample was in the range from 0.01 to 0.1 g, whereas, in the case of XRD or XRF methods, the mass of the sample was in the range of 2–6 g.

The main phases detected in the investigated ilmenites are $FeTiO_3$, Fe_2O_3, $Fe_2Ti_3O_9$, $MgTiO_3$ and $MgSiO_3$. Titanium is present only in $FeTiO_3$, $MgTiO_3$ and $Fe_2Ti_3O_9$ compounds. The thermokinetic investigation showed that the presence of $Fe_2Ti_3O_9$ phase can exert influence on the rate of the reaction. This conclusion was derived on the basis of changes of the thermal power curves shape for Norwegian ilmenite, where this phase is absent, and for Australian or Indian ilmenites, where this phase is present. The differences in thermokinetics curves between ilmenites with similar phase composition (Norwegian and Chinese)

can be explained by the presence of different phases of accompanying elements.

Therefore, on the basis of thermokinetics investigation, we can conclude that the shape of the curve of the thermal power changes is characteristic for the given raw material and can therefore be treated as its fingerprint.

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References

1. Chernet T. Applied mineralogical studies on Australian sand ilmenite concentrate with special reference to its behaviour in the sulphate process. Miner Eng. 1999;12:485–95.
2. Zhang L, Huiping H, Liao Z, Chen Q, Ta J. Hydrochloric acid leaching behavior of different treated Panxi ilmenite concentrations. Hydrometallurgy. 2011;107:40–7.
3. Zhang L, Huiping H, Wei L, Chen Q, Tan J. Hydrochloric acid leaching behaviour of mechanically activated Panxi ilmenite (FeTiO3). Sep Purif Technol. 2010;73:173–8.
4. Liu S-H, Lin C-P, Shu C-M. Thermokinetic parameters and thermal hazard evaluation for three organic peroxides by DSC and TAM III. J Therm Anal Calorim. 2011;106:165–72.
5. Lin C-P, Tseng J-M, Chang Y-M, Liu S-H, Cheng Y-C, Shu C-M. Modeling liquid thermal explosion reactor containing tert-butyl peroxybenzoate. J Therm Anal Calorim. 2010;102:587–95.
6. Jabłoński M. Investigation of thermal power of reaction of titanium slag with sulphuric acid. Cent Eur J Chem. 2010;8:149–54.
7. Klepka M, Lawniczak-Jablonska K, Jablonski M, Wolska A, Minikayev R, Paszkowicz W, Przepiera A, Spolnik Z, Van Grieken R. The composition of mineral ilmenite used in pigments production. J Alloy Compd. 2005;401:281–8.
8. Nayak PK, Das D, Chintalapudi SN, Singh P, Acharya S, Vijayan V, Chakravortty V. Quantitative multielemental analysis of titaniferous magnetites by PIXE, EDXRF, and their iron mineral characterization by Fe Mossbauer spectroscopy. J Radioanal Nucl Chem. 2002;254:351–6.
9. Jabłoński M, Przepiera A. Estimation of kinetic parameters of thermal oxidation of ilmenite. J Therm Anal Calorim. 2001;66:617–22.
10. Jabłoński M, Przepiera A. Kinetic model for the reaction of ilmenite with sulphuric acid. J Therm Anal Calorim. 2001;65:583–90.
11. Liang B, Li C, Zhang C, Zhang Y. Leaching kinetics of Panzhihua ilmenite in sulfuric acid. Hydrometallurgy. 2005;76:173–9.
12. Sasikumar C, Rao DS, Srikanth S, Ravikumar B, Mukhopadhyay NK, Mehrotra SP. Effect of mechanical activation on the kinetics of sulfuric acid leaching of beach sand ilmenite from Orissa, India. Hydrometallurgy. 2004;75:189–204.
13. Zhang G, Ostrovski O. Effect of preoxidation and sintering on properties of ilmenite concentrates. Int J Miner Process. 2002;64:201–18.
14. Piskorska E, Lawniczak-Jablonska K, Klimczyk P, Minikayev R, Paszkowicz W, Benko E, Wolska A. Quantitative phase analysis of cubic boron nitride based composites by X-ray absorption near edge structure. Spectrochim Acta B. 2007;62:461–9.
15. Klepka MT, Lawniczak-Jablonska K, Wolska A, Jablonski M. Identification of minority compounds in natural ilmenites by X-ray absorption spectroscopy. J Electron Spectrsc Rel Phenom. 2010;182:85–9.
16. Jabłoński M, Przepiera A. Hazard in reaction of titanium raw materials with sulphuric acid. J Therm Anal Calorim. 2006;83:571–3.
17. Jabłoński M. Influence of particle size distribution on thermokinetics of ilmenite with sulphuric acid reaction. J Therm Anal Calorim. 2009;96:971–7.
18. Jabłoński M. Investigation of reaction products of sulphuric acid with ilmenite. J Therm Anal Calorim. 2008;93:717–20.