

## Oxidation of Indian Ilmenite: Thermodynamics and Kinetics Considerations

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### Abstract

Natural Ilmenite ( $\text{FeO}\cdot\text{TiO}_2$ ) is the primary source for the extraction of titanium dioxide ( $\text{TiO}_2$ ). Oxidation – reduction process is used for production of synthetic rutile from ilmenite by separation of Fe-oxides from  $\text{TiO}_2$ . In this paper thermodynamics and kinetic aspects of oxidation reactions of ilmenite are discussed. Ilmenite with 53%  $\text{TiO}_2$  used for investigation is a bit different from conventional feed materials used for up-gradation processes. The slag route is generally employed for processing of low grade ilmenite with < 50%  $\text{TiO}_2$  content. Whereas high grade ilmenite with >58%  $\text{TiO}_2$  are used for production of synthetic rutile. Therefore detailed understanding oxidation – reduction behaviour of ilmenite is essential for selection and optimisation of suitable up-gradation process.

The phase equilibrium data for ilmenite oxidation reactions were computed using the FACT-Sage programme. The suitable conditions such as oxygen partial pressure, temperature, etc. for oxidation and phase separation computed using FACT-Sage program were used for experimental studies. The isothermal experiments and thermal analysis (STA) experiments were carried out to study the oxidation reactions kinetics. The mechanism of oxidation reactions of ilmenite is discussed with the help of results of experimental work and FACT-Sage computation data.

### INTRODUCTION

Titanium oxide is an important engineering material. The extent to which  $\text{TiO}_2$  is used in the day-to-day life is quite surprising, it finds applications in paints, papers, plastics, cosmetic and electronic industries. The pigment grade  $\text{TiO}_2$  is produced from titania slag and rutile (natural and synthetic) by sulphate process or chloride process. Both of these processes demand high grade feed materials to reduce the generation of process waste (Gambogi, 2004). The deposits of natural rutile are limited and depleting due to extensive mining (Nameny 2003 and Wills 2003). Therefore mineral ilmenite is used as a source of the  $\text{TiO}_2$ . Various pyrometallurgical and hydrometallurgical processes are used for up-gradation of ilmenite to synthetic rutile or titania slag (Heinz 1997, Tathavadkar et al. 2004). In most of the processes used for production of synthetic rutile, ilmenite mineral is oxidized in first step followed by partial or complete reduction of iron oxide and then separation of iron values by physical or chemical techniques. Therefore oxidation is an important process in the production of synthetic rutile.

In ilmenite, iron occurs in two different oxidation states ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) in significant amounts, and therefore, the oxygen potential is an important parameter in the oxidation reaction phase equilibria. In addition to the oxygen potential, the Fe-Ti-O system forms various compounds with range of solid solution which is a function of temperature and pressure, and therefore makes the equilibrium studies more complex. The phase relationship in Fe-Ti-O system was investigated by various research groups

(Roth et al. 1983) at different temperatures and oxygen partial pressures. The phase diagram of FeO-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> system shows phase transformation of ilmenite to hematite and rutile solid solutions at low temperature (Gupta et al. 1989). Above 1123 K temperature, rutile and hematite form pseudobrookite phase (Ghiorso and 1991).

In the oxidation process, the FeO present in the ilmenite reacts with oxygen in air and forms hematite or pseudobrookite depending on the oxygen partial pressure and reaction temperature (Gupta et al. 1989). The pre oxidation of ilmenite improves the reduction reaction of ilmenite and also helps disproportionation of iron oxide from TiO<sub>2</sub> lattice. Various impurities and gangue minerals present in the ilmenite concentrate also influence the oxidation reaction. Therefore, thermodynamics aspects of the oxidation reactions were investigated using FACT-sage thermodynamic computation software (FACT 2004) and reaction kinetics was studied by using thermal analysis and isothermal oxidation reaction experiments.

## **EXPERIMENTAL WORK**

Ilmenite concentrates beneficiated from heavy mineral sand deposits of Tamilnadu at the R & D laboratory of Tata Steel were used for present studies. The chemical composition of the ilmenite samples was analysed by wet chemical and ICP-OE spectrophotometer. The phases in ilmenite were examined by JEOL JXA-6400 scanning electron microscope attached with KEVEX superdry, Energy-Dispersive X-ray detector (EDX).

### **Thermal Analysis**

The oxidation reactions of ilmenite samples were investigated by using Netzsch STA 409C Simultaneous Thermal Analyzer (STA). The  $\alpha$ -alumina powder was used as a reference material. A 20-mg sample of ilmenite concentrate and a reference sample were weighted accurately and then placed inside the sample and reference cells, respectively. The STA experiments were carried out in air. The data were collected using a PC-based data acquisition and processing system. The phase changes were recorded in the form of thermograms showing the endothermic / exothermic (DSC) and weight gain / loss (TGA) events for the 10 C/min scan. The phases formed in ilmenite samples after oxidation reactions were characterized by various techniques.

### **Isothermal Heat Treatment**

The ilmenite concentrate samples were heat treated isothermally in the temperature range of 973 to 1273 K in air. Two grams of concentrate were weighed accurately and transferred into a 20-ml alumina crucible. The crucible was then charged in the preheated furnace and 500 ml/min air flow was maintained throughout the experiment. The sample temperature was recorded using a Pt/Pt13 pct Rh thermocouple. The selection of soaking time was based on the common industrial practice used for oxidation reaction. The weights of the samples before and after experiments were measured to calculate the weight gained due to oxidation reaction. For electron microscopic examination, a vacuum impregnation method was used for mounting the samples in resin. The samples for microscopic examination were prepared by grinding with emery paper followed by polishing with diamond paste. Polished samples were examined using a scanning electron microscope (JEOL JXA-6400 series), which was operated at 15 kV accelerating voltage. The semi quantitative analysis of various phases was carried out using, KEVEX superdry, EDX detector. The part of the samples was used for X-ray Diffraction analysis by Philips Diffractometer.

## **RESULTS AND DISCUSSION**

The chemical composition of the ilmenite is given in Table 1. The microstructure and EDX phase analysis of ilmenite are shown in Figure 1. The microstructure shows primarily grains of well-defined ilmenite (bright phase), rutile (light grey phase) and a small quantity of siliceous gangue (dark gray phase).

Table 1: Chemical Composition of Ilmenite Concentrate

Compound	TiO <sub>2</sub>	FeO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Mn	Cr
Concentration in Wt%	53.50	30.10	13.80	0.34	0.51	0.05	0.72	0.32	<0.05

(Concentration in Wt. %)

	O(Ka)	Al(Ka)	Si(Ka)	Ti(Ka)	Fe(Ka)	Zr(La)
Grain 1	27.19	0.13	0.19	38.78	33.38	0.33
Grain 2	27.46	0.11	0.19	38.93	33.12	0.18
Grain 3	26.96	0.20	0.14	39.15	33.32	0.23

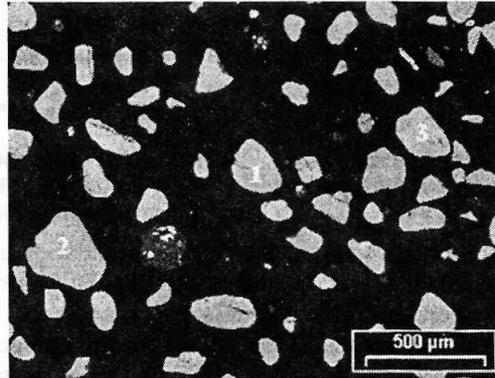
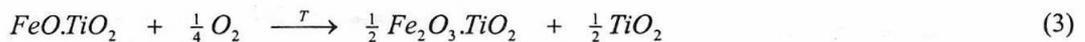
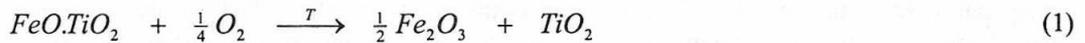


Fig. 1: Microstructure and EDX Phase Analysis of Ilmenite Concentrate

### Thermodynamics Consideration

The SEM micrographs and EDX analysis of ilmenite show the variation in Fe content in both rutile and ilmenite. Possible oxidation reactions of ilmenite are as follows:



The change in free energy of these oxidation reactions was calculated using the FACT-Sage 5.4 program and a plot of free energy change ( $\Delta G$ ) against temperature ( $T$ ) is shown in Figure 2. It is evident from Figure 2 that at low temperatures, formation of hematite and rutile is thermodynamically more favorable as reaction 1 is having lower DG value than reactions 2 and 3, where as above 1110 K (837 C) temperatures, pseudobrookite ( $Fe_2TiO_5$ ) and rutile are more stable phases in oxidizing atmosphere. *Equilib* module of FACT-Sage programme is based on free energy minimization (Bale et al. 2002). Oxidation phase equilibria of ilmenite were computed using *Equilib* module in FACT-Sage 5.4 programme. The oxide constituents (as given in Table 1) of the 100 gm ilmenite concentrates were used as input for the computation and the oxygen concentration was varied for computation of phase equilibria at different temperatures. The effect of temperature on ilmenite oxidation phase equilibria at  $P_{O_2} = 1$  atmosphere is presented in Figure 3, which shows that below 1073 K temperature, rutile ( $TiO_2$ ), hematite ( $Fe_2O_3$ ), and small fraction of ilmenite ( $FeTiO_3$ ) are stable phases. Above 1073 K temperatures, hematite and part of rutile transform to pseudobrookite ( $Fe_2TiO_5$ ). The ilmenite concentration increases with temperature and reaches to ~ 2% (2 gm in 100 gm ilmenite concentrate) at the transition temperature and then drops down with rise in temperature.

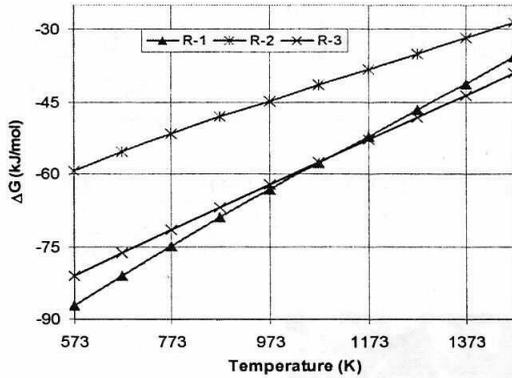


Fig. 2: The Plot of Free Energy Change ( $\Delta G$ ) Against Temperature (T) for Oxidation Reactions of Ilmenite as Given in Text

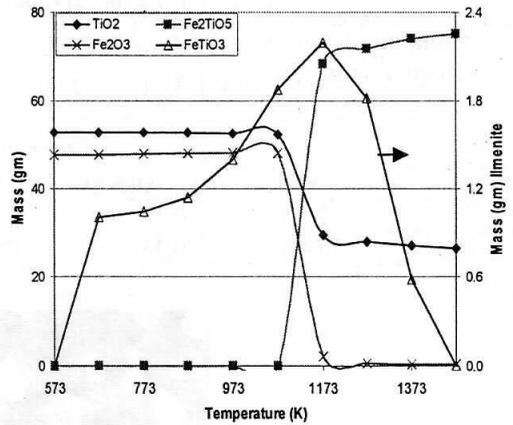
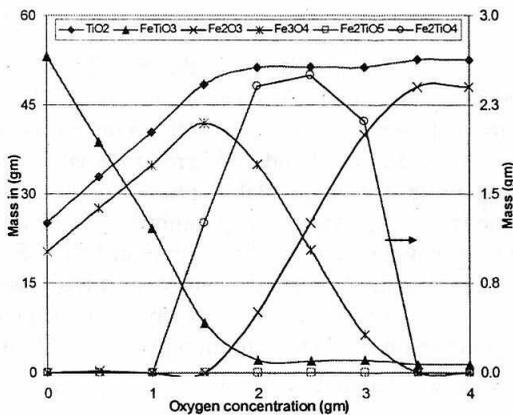
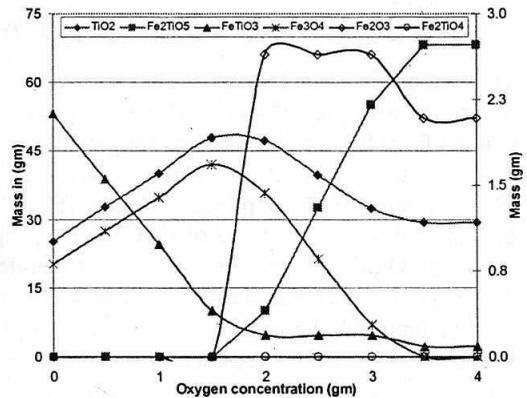


Fig. 3: Effect of Temperature on Ilmenite Oxidation Phase Equilibria at  $P_{O_2} = 1$  Atmosphere Pressure Computed using Fact-Sage 5.4

The plot of amount of phases formed versus input oxygen concentration in the system at 973 and 1173 K temperatures are presented in Figures 4a and b. At 973 K temperature, which is below the pseudobrookite formation temperature, mass of rutile phase increased in range of 0 to 2 gm input oxygen level and above 2 gm oxygen there was no significant change the mass of rutile formed. Whereas at 1173 K, the concentration of rutile decreased after 2 gm oxygen input due to formation of pseudobrookite phase. In the both figures 4a and b, the magnetite was stable phase at lower oxygen level and above 1.5 gm oxygen input hematite and magnetite phases were formed. It was also observed from Figure 4b, that for pseudobrookite formation minimum 2 % input oxygen mass is required even at 1173 K. Thus formation of pseudobrookite is function of temperature and oxygen partial pressure. The phase equilibria computations also revealed that below pseudobrookite formation temperature, small fraction of rutile is also transforms to ulvospinel ( $Fe_2TiO_4$ ) phase at lower oxygen partial pressure. Thus, depending on the reaction temperature and oxygen partial pressure, various products such as hematite, magnetite, rutile, ilmenite, pseudobrookite, and ulvospinel are formed



(A) T = 973 K



(B) T = 1173 K

Fig. 4: Effect of Oxygen Concentration on Ilmenite Oxidation Phase Equilibria at (A) 973 K and (B) 1173 K Temperatures, Computed Using Fact-Sage 5.4

during oxidation of ilmenite. Since reduction behavior (rate and mechanism) of these compounds is different, it is necessary to optimize the oxidation reactions parameters to produce the required oxidation products. It was concluded from the results of computation that for oxidation of ilmenite and formation of rutile and hematite phases the thermodynamically favorable conditions are 1073 K reaction temperature and 2% oxygen concentration in the charge input.

### Thermal Analysis

The STA thermograms of oxidation of ilmenite concentrate in Figure 5. The weight loss step (AB) in the TGA curve in the temperature range of 373 to 523 K is due to loss of moisture in the samples and silicate gangue phases. The DSC curve shows an endothermic peak (a) in the same temperature region. The weight loss event is followed by a small weight gain step (BC) until 650 K and then no change in the weight (step CD) is observed until temperature reaches 773 K. Small exothermic peak (b) was observed at 573 K in DSC curve which is due to oxidation of primary FeO. In the temperature range between 573 K and 1173 K (DEF), the rate of weight gain is larger than step CD with a step change at around 973 K (E). The DSC curve shows two distinct endothermic peaks in this temperature range, the first peak (c) indicate the formation of Fe<sub>2</sub>O<sub>3</sub> and second large peak, d, indicates the formation of pseudobrookite, as discussed earlier. The stoichiometric value of weight gain due to the oxidation of FeO to Fe<sub>2</sub>O<sub>3</sub> in an oxidizing atmosphere was calculated from the following reaction:

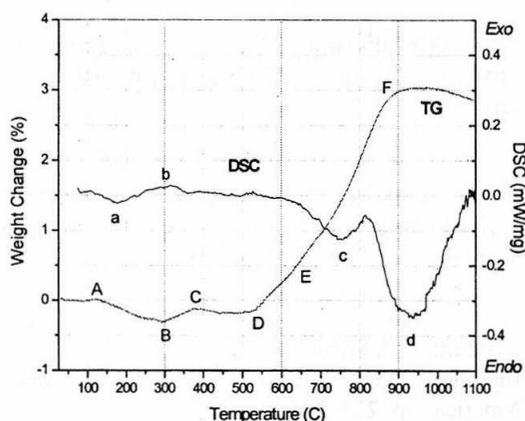


Fig. 5: Thermographs of Ilmenite Oxidation Reaction Analyzed by using Sta

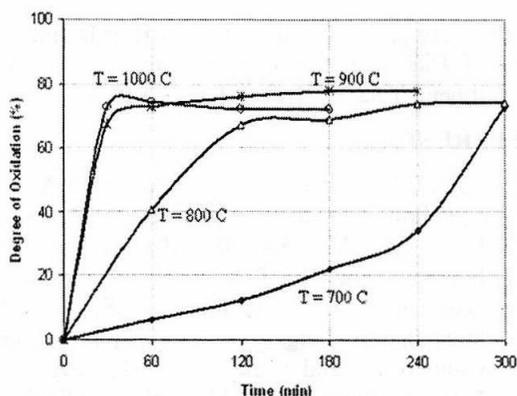


Fig. 6: The Graph of % Degree of Oxidation Against Soaking Time at Different Temperatures

The analyzed FeO content in Indian ilmenite is 30.10%, from which the corresponding stoichiometric weight gain due to the oxidation of FeO is 3.45 %. The total weight gain observed from the TGA curve in Figure 5 is approximately 3.35% in air, which agrees with the value of weight gain calculated from Eq. (4).

### Isothermal Heat Treatment

The graph of % degree of oxidation i.e. the ratio of weight gain to theoretical weight gain, at against soaking time at different temperature is presented in Figure 6. The Figure 6 shows the effect of time and temperature on the degree of oxidation of ilmenite. The rate of oxidation is very slow at 973 K initially and then increased above 4 hours soaking time. At 1073 K isothermal oxidation reaction shows steady increase in the rate of reaction for first 2 hours and then very small incremental increase was observed. About 70 % degree of oxidation was achieved in less than one hour at 1173 K and 1273 K due to high temperatures. The degree of oxidation increased further to ~ 80% for 1173 K

temperature curve whereas small weight loss was observed in case of 1273 K curve. This weight loss might be due to decomposition of  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ . The XRD analysis revealed the presence of rutile, hematite, magnetite and ilmenite when heat treated in air at 973 K, whereas a distinct pseudobrookite phase was observed in XRD pattern of 1173 K sample. The discrete Fe-rich phases were also confirmed in the microstructure of samples oxidized at 1173 K whereas Fe-rich and Ti-rich regions were present in the samples oxidized at 973K.

## CONCLUSIONS

The oxidation of ilmenite is a complex phase transformation process depending on the oxygen partial pressure and temperature. The oxidation reactions can be explained by thermodynamic phase equilibria computation and thermal analysis data. In an oxidizing atmosphere, the oxidation of FeO in ilmenite promotes the formation of hematite and rutile below 1073 K, which then transforms into a pseudobrookite phase at high temperatures. The experimental (TGA) and calculated values of weight gain due to the oxidation of FeO in air are comparable. The phase and structural transformation in the ilmenite phase in an oxidizing atmosphere has a profound influence on the kinetics of the processes used for the production of synthetic rutile *via* the carbothermic reduction. The observed phase transformation in ilmenite generates vacancies during the oxidation of FeO, which aids the diffusion of cations during reduction reactions and thereby increases the reactivity of the reactants during the reduction reaction.

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