Thermogravimetry studies on ilmenite nitridation

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Abstract

The present study is based on the possibility of beneficiation of Indian-ilmenite by carbonitrothermic process. The investigations were carried out in two parts. In the first part, thermogravimetric-differential thermogravimetric (TG-DTG) experiments were conducted using cold pressed pellets of blended mixtures TiO_2-C and $FeTiO_3$-C. The TG experiments were carried out up to 1500 °C at the rate of 10 °C/min under flowing nitrogen gas. The formations of TiN in case of TiO_2-C mixture and TiN along with Fe in case of $FeTiO_3$-C mixture were observed. In the second part, the experiments were conducted using similar pellets, prepared under identical conditions, in a resistance heating furnace at 1500 °C. By simple operations of crushing and sieving, the products obtained from the ilmenite-carbon mixture were separated into a fraction enriched in titanium and a fraction depleted in titanium.

*Keywords: ilmenite, beneficiation, TiO_2, thermal analysis*

I. Introduction

Ilmenite ($FeTiO_3$) and rutile (TiO_2) are well-known minerals of titanium [1]. The TiO_2 content in ilmenite is considerably smaller than in rutile due to the presence of iron. Hence, it is necessary to upgrade ilmenite (enhance TiO_2 content) by removing iron (oxide) before it could be processed for recovery of pure TiO_2 or Ti-metal. In India, there is an abundance of titanium-based deposits, equivalent to about 15% of the total world titanium resources, in the form of major titanium minerals ilmenite and rutile [1–4]. The deposits of ilmenite ($FeTiO_3$, 43–60% TiO2) are more plentiful (130 million tonnes) than the reserves (7–10 millon tones) of rutile (92–96% TiO_2). While the higher TiO_2 content of rutile makes it suitable for direct chlorination and subsequent processing to metal or high quality pigment grade titanium dioxide, the considerable iron content in ilmenite necessitates its processing by a variety of beneficiation techniques before chlorination [5–11]. In this connection, a number of techniques have been used [12–17], some of them at major industrial scale, to beneficiate ilmenite all over the world. However, there are technical or economic limitations associated with each of these techniques and with respect to the type of ilmenite

being processed because the mineralogical characteristics of ilmenite are different depending on the location of the deposits. The search for improved and new processes for beneficiation of ilmenite continues [15–18] and the present study provides a potential and effective process that could be used on a large scale. The possibility of using nitridation as the key process for beneficiating ilmenite was revealed in our laboratory during the systematic investigations of carbonitrothermic process for converting group IV and V metal oxides to nitrides [1,18]. The reaction was extensively investigated by TG-DTG for both titanium dioxide and ilmenite and comparative results of carbonitrothermic reduction are described in detail. From the obtained results the cost-effective beneficiation process could be developed.

II. Experimental

Stoichiometric amounts (defined by equation 1) of titanium dioxide (99.89% TiO_2) and graphite powder (99.95% pure) were blended together.
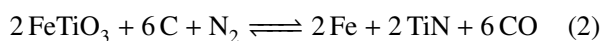
$$2\,TiO_2 + 4\,C + N_2 \rightleftharpoons 2\,TiN + 4\,CO \qquad (1)$$
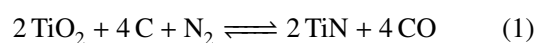
The prepared TiO_2-C mixture was compacted to a pellet of 12 mm diameter using uniaxial cold pressing by applying hydraulic pressure of 10 tons. A small portion (80–100 mg) of the prepared pellet was heated in thermoanalyser (TAG 24 Setaram) at the heating rate of

10 °C/min up to 1500 °C under flowing nitrogen at the rate of 2 L/h. In another experiment 50 g of the prepared pellet was loaded in a molybdenum lined alumina crucible and heated up to 1500 °C in a $MoSi_2$ resistance heater under flowing nitrogen gas.

In the second part of the investigation, ilmenite and graphite powder (99.95% pure) in stoichiometric amounts (defined by equation 2) were blended together.

$$2\,FeTiO_3 + 6\,C + N_2 \rightleftharpoons 2\,Fe + 2\,TiN + 6\,CO \quad (2)$$

The prepared $FeTiO_3$-C mixture was compacted to pellets of 12 mm diameter using uniaxial cold pressing by applying hydraulic pressure of 10 tons. In this case two types of experiments were also conducted under identical conditions as for the TiO_2-C charge.

Phase composition of the precursor powders ($FeTiO_3$ and TiO_2) and their products after carbonitrothermic reduction were analysed by X-ray diffraction (XRD) using Philips (Make) XRD machine with Cu K_α radiation.

III. Results and discussion

Thermal analysis (TG and DTG) result of the pellet prepared from the TiO_2-C mixture is presented in Fig. 1. The sample starts losing weight above 1050 °C indicating that the reaction begins at this temperature. Weight loss is continuous during the course of experiment and at the end of heating (at 1500 °C for about 3.5 hours) the sample losses weight corresponding to 96% of the total loss expected for the complete reaction. Even though titanium forms many oxides (TiO_2, Ti_3O_5, TiO) [1] there are only two differential thermogravimetric (DTG) peaks in the DTG plot (Fig. 1). According to Krishnamurthy *et al.* [2] in the investigated temperature range minimum three peaks can be expected [2], indicating that at least two of the peaks merge together. If the mass balance is calculated, the expected weight loss for conversion of TiO_2 to Ti_3O_5 is 11 wt.% and for the conversion of TiO_2 to TiO through Ti_3O_5, it is 30.5 wt.%. The weight loss in the sample up to 1335 °C, corresponding to the end of the first of the two DTG peaks, is 32 wt.%. It is clear that the conversion of TiO_2 to Ti_3O_5 and further to TiO occurs between 1050 °C and 1335 °C. The peaks corresponding to each of these two steps overlap and show up as a single peak in the thermogram presented in Fig. 1. The second peak corresponds to the reaction as shown by equation 3, which begins at 1335 °C and is still continuing even at 1500 °C.

$$2\,TiO + 2\,C + N_2 \rightleftharpoons 2\,TiN + 2\,CO \quad (3)$$
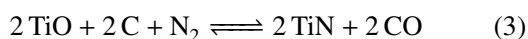
The maximum rate of weight loss due to this reaction is found to occur at 1435 °C, the temperature corresponding to the second DTG peak in the plot (Fig. 1). Prolonging the treatment at 1500 °C drives the overall reaction to 96% completion at the end of 3.5 hours. It was independently confirmed by an experiment in the resistance heating furnace that the reaction quickly precedes the completion on further heating the charge to 1700 °C.
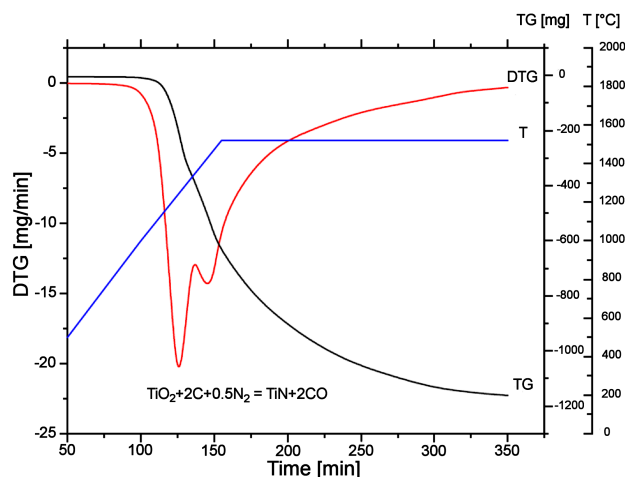

Figure 1. Carbonitrothermic reduction of titanium dioxide analysed by TG and DTG

The conversion of TiO_2 to TiN cannot occur by a reaction between the oxide and nitrogen alone because each of the many binary oxides formed by titanium is more stable than the nitride [1,2]. It is known [1,2] that titanium forms many stable oxides in the solid state and the reduction of TiO_2 to metal has to proceed through the sequential formation of lower oxides. The lowest oxide is TiO and any calculation on the feasibility of the overall reaction is the best assessed by calculating the free energy change for reaction 3. Carbonitrothermic conversion of titanium oxide to titanium nitride, represented by reaction 3 is thermodynamically feasible even at moderate temperature of about 500 °C [1]. The feasibility of the carbothermic processes improves with the rise in temperature, due to the well known increase in the stability of carbon monoxide with increase in temperature. The carbothermic reductions occur fast and the required total processing time is much lower compared to reactions involving ammonia. One of the major considerations in the use of the carbothermic processes is the possibility of parallel and side reactions. The reaction between carbon and titanium oxide can lead to formation of other products such as titanium carbide, the metal itself or a product consisting of solid solutions of these compounds such as carbonitrides. The conditions can however be chosen suitably to steer the reaction towards the desired end product, in this case, the nitride. The standard free energy change of reaction between titanium oxide and carbon resulting in the formation of titanium carbide, as shown in equation 4, is negative above about 1100 °C [1].

$$TiO + 2\,C \rightleftharpoons TiC + CO \quad (4)$$

This temperature is considerably higher than the calculated minimum temperature (500 °C) for nitride formation. Besides, Gibbs free energy − temperature ($\Delta G_R^0 - T$) slope of the carbide line is larger than the nitride line [1,2], and the carbide formation reaction becomes more and more feasible with increase in temperature. Thus, titanium nitride formation is more favoured

and the nitride could be the expected product at relatively lower temperatures, whereas, if sufficient carbon was present, the carbide formation will be more pronounced at higher temperatures. When both nitride and carbide can be formed with almost equal feasibility, there is a possibility for the formation of carbonitride. This is another process with a negative free energy change. In other words, the carbonitride formation is associated with a larger negative free energy of reaction than the formation of either the carbide or nitride alone. This tendency can also manifest as carbon present as the impurity in the nitride if sufficient quantity is not present for outright carbide formation. By stoichiometry, one can expect residual oxygen also in the product. These features do not affect the process in a major way or its intended use.

The carbonitrothermic reduction of illmenite was investigated under identical conditions. Many reaction steps could also be anticipated in the thermogravimetric pattern of the illmenite-carbon ($FeTiO_3$-C) mixture during the course of heating between room temperature and 1500 °C [2]. However, in DTG curve (Fig. 2) only two large peaks are observed. The reaction and hence weight loss begins at 690 °C and, as in the previous case (TiO_2-C mixture), many reaction steps are overlapped leading to the merging of DTG peaks. The weight loss up to 1150 °C, i.e., the step marked by the first DTG peak, is 5.4 wt.%. By examining possible mass balances in the charge, it can be inferred that the reaction in this temperature range is essentially reduction of the iron oxides to iron or iron nitrides. In a separate study [1] on nitridation of ferroniobium with ammonia at 950 °C, it has been found that Fe_2N and Fe_4N phases are present in the nitrided product. The temperature and gas environment conditions being similar in the present case, presence of nitrides of iron in the product at 1150 °C, should not be ruled out. Iron nitrides are not very stable compounds and undergo decomposition at higher temperature [1,18]. The second and large DTG peak in Fig. 2 is the result of many overlapping processes, including the
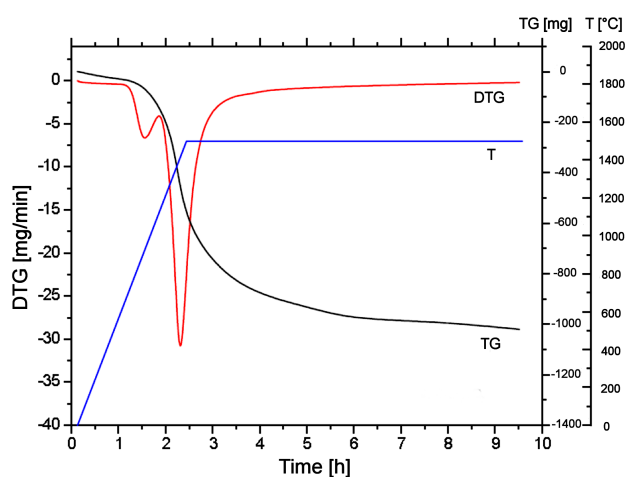
decomposition of iron nitrides [1] and reduction of TiO_2 to Ti_3O_5, Ti_3O_5 to TiO and of TiO to TiN. It is interesting to note that the peak temperature of the second DTG peak is exactly the same in Figs. 1 and 2, i.e., 1435 °C. This can be attributed to the reaction step represented by equation 2. Thus, this reaction occurs at the same temperature for the pure TiO_2 precursor material and also for illmenite, which indicates that the state of TiO (the activity of TiO in the reacting mass) at the moment reaction 3 would occur is identical. It should be noted that the same cannot be said about the first step of titanium oxide component reduction in the pure TiO_2 and in illmenite. In the pure TiO_2, the first step of titanium oxide component reduction begins at 1050 °C, as evident from Fig. 1. In illmenite, first step of titanium oxide component reduction begins at 1150 °C, as evident from Fig. 2. This is to be anticipated because in illmenite, titanium oxide is bound to iron oxide and the activity of titanium oxide undergoing reaction with carbon in the first stage is less than one. In pure titanium oxide, the activity of titanium oxide undergoing reaction with carbon in the first stage is one.

The starting materials (TiO_2 and illmenite) and the products of the carbonitrothermic reduction at 1500 °C were analysed by XRD to identify phases present and the results are shown in Figs. 3 and 4. XRD patterns presented in Fig. 3 confirm that rutile and $FeTiO_3$ are dominant phases in TiO_2 and illmenite, respectively. As illustrated in Fig. 4 (pattern b), the product of the carbonitrothermic reduction TiO_2, as starting material, contained TiN as the only phase. After the carbonitrothermic reduction of illmenite TiN and Fe phases are formed (Fig. 4, pattern a). This is obvious, because the investigation was carried out at 1500 °C and at this temperature iron nitride is not stable.

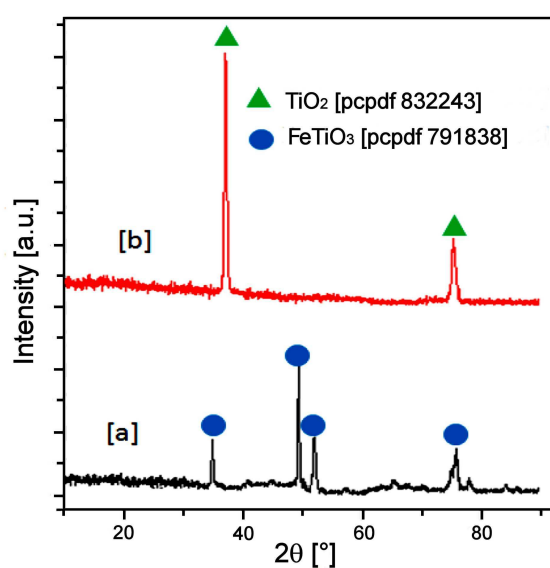One of the major objectives of the investigation is to use nitridation as a process to beneficiate illmenite,

Figure 2. Carbonitrothermic reduction of illmenite ($FeTiO_3$) analysed by TG and DTG

Figure 3. XRD analysis of calcined starting materials: a) illmenite ($FeTiO_3$) and b) TiO_2
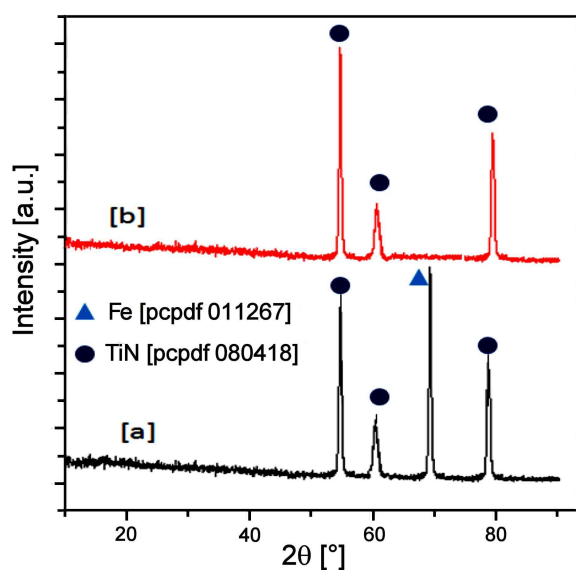
**Figure 4. XRD analysis of carbonitrothermic products of:
a) ilmenite (FeTiO$_3$) and b) TiO$_2$**

since the obtained iron and TiN can be readily separated. Titanium nitride is hard and brittle, while iron is soft and malleable. The investigation process aimed at using this difference in properties. The product from the nitridation of ilmenite, obtained in resistance heating (with MoSi$_2$ heating element) furnace at 1500 °C, was crushed. Titanium nitride part crushed to a fine powder and iron component remained coarse. The crushed product was separated into fine and coarse fractions by sieving. As expected the finer sieves fraction contained more of titanium nitride and the coarser sieve fraction contained more of iron, relative to the starting ilmenite material. Thus, the Ti/Fe ratio in the starting ilmenite material, finer fraction and coarser fraction is 1.77, 2.83 and 1.37, respectively. These preliminary results have been greatly improved by further work in the process from the beneficiation point of view and will appear in a separate publication dealing with minerals processing.

IV. Conclusions

The nitridation of TiO$_2$ and ilmenite (FeTiO$_3$) by carbonitrothermic reduction was investigated by thermogravimetry. The pure TiO$_2$ yielded TiN at 1500 °C, but the reaction proceeded to only 96% completion even after 3.5 h. Due to this, residual carbon and hence oxygen were the impurities in the obtained nitride. As revealed by the DTG pattern the overall reaction occurs in two major steps, the first corresponding to the conversion of TiO$_2$ to TiO through Ti$_3$O$_5$, and the other corresponding to the conversion of TiO to TiN. In the case of ilmenite, the first step, starting at much lower temperature than expected for TiO$_2$ reaction corresponds to the reduction of iron oxides and the second DTG peak represented the processes for the conversion of TiO$_2$ to TiN through the intermediate oxides Ti$_3$O$_5$ and TiO. A shift in the reaction temperature to higher values was also

observed when the reacting component, titanium dioxide, is bound in the start material as in ilmenite, but once the component is liberated during the course of reaction, the reaction occurs at the same temperature irrespective of the nature of the original starting material. The possibility of using nitridation for beneficiation of ilmenite was also indicated by experimental results.

References

1. A.K. Suri, *Studies on processing of some rare metal resources*, Ph.D. Thesis, University of Mumbai, India, 1991.
2. N. Krishnamurthy, S. Kumar, A. Mukherjee, S.P. Garg, "Thermogravimetry studies on ilmenite nitridation", pp. 157–160 in *15th National Symposium of Thermal Analysis (Thermans)*, Indian Thermal Analysis Society, Jaipur, 2006.
3. B. Charlier, J.C. Duchesne, J. Vander Auwera. "Magma chamber processes in the Tellnes ilmenite deposit (Rogaland Anorthosite Province, SW Norway) and the formation of Fe–Ti ores in massif-type anorthosites", *Chem. Geol.*, **234** (2006) 264–290.
4. K. Swaminathan, C.H.S. Rao, "Chloridization beneficiation of ilmenite", *Metall. Mater. Trans. B*, **15** (1984) 259–275.
5. R.C. Behera, A.K. Mohanty, "Beneficiation of massive ilmenite by froth flotation", *Int. J. Miner. Process.*, **17** (1986) 131–142.
6. G. Chen, Z. Song, J. Chen, J. Peng, C. Srinivasakannan, "Evaluation of the reducing product of carbonthermal reduction of ilmenite ores", *J. Alloys Compd.*, **577** (2013) 610–614.
7. D. Filippou, G. Hudon, "Iron removal and recovery in the titanium dioxide feed-stock and pigment industries", *J. Miner. Metal. Mater. Soc.*, **61** (2009) 36–42.
8. N.J. Welham, J.S. Williams, "Carbothermic reduction of ilmenite (FeTiO$_3$) and rutile (TiO$_2$)", *Metall. Mater. Trans. B*, **30** (1999) 1075–1081.
9. X. Xiong, Z. Wang, F. Wu, X. Li, H. Guo, "Preparation of TiO$_2$ from ilmenite using sulfuric acid decomposition of the titania residue combined with separation of Fe^{3+} with EDTA during hydrolysis", *Adv. Powder Technol.*, **24** (2013) 60–67.
10. K.C. Liddell, "A model for the recovery of titanium from mixtures of ilmenite and hematite by hydrochloric acid leaching", *Sep. Sci. Technol.*, **23** (1988) 2005–2014.
11. A.J. Easteal, A.T. Morcom, "Recovery of titanium dioxide from naturally occurring ilmenite by high-temperature borate fusion", *J. Chem. Technol. Biotechnol.*, **30** (1980) 481–484.
12. R.K. Biswas, M.A. Habib, N.C. Dafader, "A study on the recovery of titanium from hydrofluoric acid leach solution of ilmenite sand", *Hydrometall.*, **28** (1992) 119–126.
13. S.A. Rezan, G. Zhang, O. Ostrovski, "Carbothermal reduction and nitridation of ilmenite concentrates",

ISIJ Int., **52** (2012) 363–368.

14. N.J. Welham, P.E. Willis, "Formation of TiN/TiC–Fe composites from ilmenite (FeTiO$_3$) concentrate", *Metall. Mater. Trans. B*, **29** (1998) 1077–1083.

15. J.J. Swanepoel, D.S. Van Vuuren, M. Heydenrych, "Leachibility of nitride ilmenite in hydrochloric acid", *J. Sout. Afr. Inst. Min. Metall.*, **111** (2011) 137–140.

16. Y.I. Gerasimov, A.N. Krestovnikov, A.S. Shakhov, *Chemical Thermodynamics in Nonferrous Metallurgy. Volume III – Thermodynamics of Tungsten, Molybdenum, Titanium, Zirconium, Niobium, and Tantalum and of their more Important Compounds*, (Translated from Russian) The National Aeronautics and Space Administration U.S.A. & The National Science Foundation, Washington DC, 1965.

17. M.A.R. Dewan, G. Zhang, O. Ostrovski, "Phase development in carbothermal reduction of ilmenite concentrates and synthetic rutile", *ISIJ Int.*, **50** (2010) 647–653.

18. H.O. Pierson, *Handbook of Refractory Carbides and Nitrides: Properties, Characteristics, Processing and Applications.* Ed. W. Andrew, Elsevier, 1996.