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Effect of carbon on the beneficiation of OSCOM ilmenite by carbonitrothermy

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ABSTRACT

Ilmenite ($FeO{\cdot}TiO_2$) and rutile (TiO_2) are well-known minerals for titanium. Ilmenite is far more abundant than rutile in nature. However, ilmenite contains iron oxides and the TiO_2 content of ilmenite is considerably less than rutile. Hence it is necessary to upgrade (enhance TiO_2 content) Ilmenite by removing iron before it could be processed for recovery of pure TiO_2. Compared to the other grades of ilmenite in India, OSCOM grade from Chatrapur, Orissa has the lowest content of TiO_2. Hence beneficiation of such a grade of ilmenite is highly challenging and cost intensive. The present work explores the possibility of beneficiation of ilmenite by a carbonitrothermic process using three different forms of carbon namely, petroleum coke, carbon black and graphite. The thermogravimetry results of carbonitrothermic reduction of ilmenite and rutile and the residue analysis are presented in detail to determine whether the form of carbon has any role in this beneficiation process.

1. Introduction

India is rich in titanium mineral reserves and is home to about 15% of the total world titanium resources, in the form of major titanium minerals ilmenite and rutile. The deposits of ilmenite ($FeO{\cdot}TiO_2$, 43–60% TiO_2) are plentiful (130 million tons) than the reserves (7–10 millon tons) 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 of ilmenite necessitates its processing by a variety of beneficiation techniques before it is ready for chlorination. The titanium mineral deposits occur in India at Chavara in Kerala, Manavalakurichi in Tamil Nadu and Chatrapur in Orissa. Orissa ilmenite is also known as OSCOM ilmenite (after Orissa Sands Complex). Compared to the other grades of ilmenite, OSCOM grade from Chatrapur, Orissa, India has the lowest content of TiO_2 [1]. Hence beneficiation of OSCOM grade of ilmenite is highly challenging and cost intensive [2]. Several techniques of beneficiation used for Indian ilmenite are documented in a review by Rao [3]. Beneficiation of ilmenite in general has been done by many techniques over the years [4–12]. The present work focuses on the carbothermic nitrization of ilmenite. Work on nitridation of ilmenite has been recently reported [13,14]. However, as per our knowledge no extensive work has been reported on the carbonitrothermic reduction of ilmenite. The possibility of using nitridation as the key process for beneficiating ilmenite was revealed during our earlier investigations and also by a work by Swanepoel et al. [15,16]. In the carbonitrothermic process, the metal oxide is reacted with carbon in a nitrogen atmosphere at high temperatures. Titanium values convert to the nitrides and oxygen is removed from the charge as carbon monoxide while iron oxides reduce to metal. The overall reaction is represented by

$$FeO{\cdot}TiO_2 + 3C + 0.5N_2 = Fe + TiN + 3CO \tag{1}$$

In this work, beneficiation of OSCOM grade ilmenite was done by carbonitrothermy with three different forms of carbon, namely, petroleum coke, carbon black and graphite. Among the forms of carbon used, both petroleum coke and carbon black are cheaper compared to graphite. However, petroleum coke made by carbonizing process of crude oil distillation residues contains high amount of sulfur (around 7%) [17] and carbon black formed as soot under normal combustion conditions are relatively impure when compared to graphite.

The present paper explores the possibility of beneficiation of ilmenite by a carbonitrothermic process using these three forms of carbon. The thermogravimetry results of carbonitrothermic reduction of ilmenite and rutile and the residue analysis along with phase analysis are presented in detail to determine whether the form of carbon has any role in this beneficiation process.

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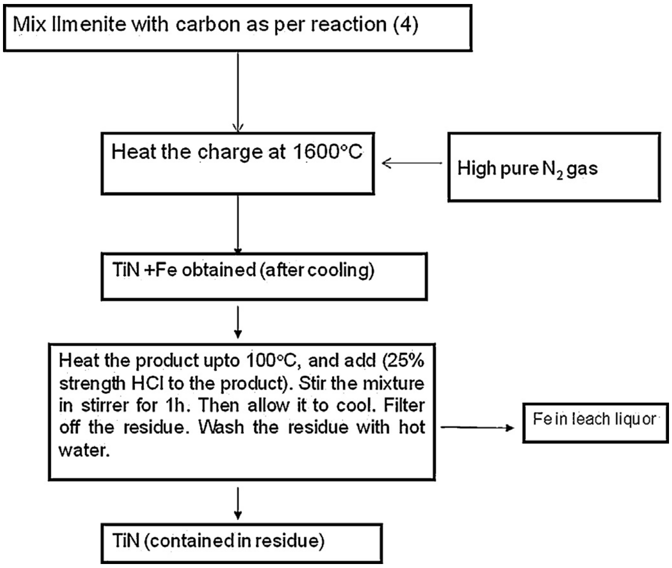

Fig. 1. Flowsheet of the carbonitrothermy process used in the present study.

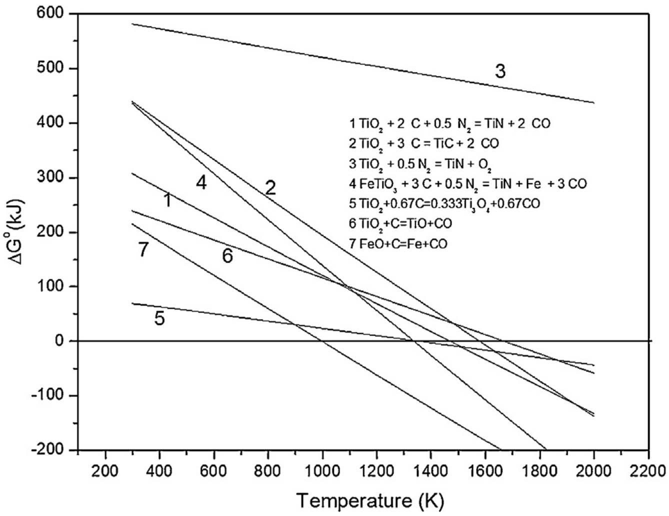

Fig. 2. Free energy of different reactions used in the study. Calculated using FACT-SAGE software.

2. Carbonitrothermy process

A detailed flowsheet of the carbonitrothermy process reported in this paper is illustrated in Fig. 1.The thermodynamics feasibility of all the reactions discussed in this paper is shown in Fig. 2. Fig. 2 was constructed using FACT 53 databases in FACTSAGE 6.5 software. As could be seen in Fig. 2, direct conversion of titanium dioxide to titanium nitride by a reaction between the oxide and nitrogen alone is not possible (line 3 of Fig. 2). This is because each oxides formed by titanium are in fact more stable than the nitride. The preparation of nitride from titanium dioxide will therefore involve a more complex reaction. In this context, the following reaction may be examined:

$$TiO_2 + 2C + 0.5N_2 = TiN + 2CO \tag{2}$$

The reaction shown above involves a combination of reduction and nitridation. Carbonitrothermic conversion of titanium oxide to titanium nitride, represented by reaction (2) is thermodynamically feasible at temperatures of about 1180 °C (1453 K) (line 1 of Fig. 2).

The feasibility of only carbothermic process improves with rise in temperature (around 1300 °C free energy of such a reaction is negative (line 2 in Fig. 2)), due to the well-known increase in the stability of carbon monoxide with increase in temperature. Thus one of the major considerations in the use of carbonitrothermic processes is the possibility of parallel and side reactions. The reaction between carbon and titanium oxide can lead to the formation of other products such as titanium carbide or a product consisting of solid solutions of these compounds such as the carbonitrides. The conditions can, however, be chosen suitably to steer the reaction toward the desired end product, in this case, the nitride. The following information is thus useful.

Table 1
Various reactants used in the study (all are in wt%).

1	OSCOM ilmenite	50% TiO_2, 34% FeO and 16% Fe_2O_3
2	OSCOM rutile	95% TiO_2, 0.9% SiO_2, 1.1% Fe_2O_3, 0.8% ZrO_2
3	Petroleum coke	88% carbon with 9% of volatile materials and 3% S
4	Carbon black	95.7% carbon, 1% S, 3.1% O, 0.2% N, 200 mg/kg Na.
5	Graphite powder	99.95% pure carbon

The standard free energy change of reaction between titanium oxide and carbon resulting in the formation of titanium carbide,

$$TiO_2 + 3C = TiC + 2CO \tag{3}$$

is negative above about 1300 °C. This temperature is considerably higher than the calculated minimum temperature (1180 °C) for nitride formation. Besides, the slope of the carbide ($\Delta G^\circ - T$) line is larger than the nitride line, and the carbide formation reaction becomes more and more feasible with increase in temperature. Thus, titanium nitride formation is more favored and the nitride shall be the expected product at relatively lower temperatures, whereas, if sufficient carbon were present, the carbide formation will be more pronounced at higher temperatures. When both nitride and carbide can form with almost equal feasibility, there is a possibility for formation of carbonitride [13]. This is another process with a negative free energy change.

3. Experimental

The compositions of the starting materials are shown in Table 1. Stoichiometric amounts of OSCOM grade ilmenite and stoichiometric amount of petroleum coke, carbon black and graphite powder were mixed according to Eq. (4) and compacted to pellets.

$$2FeO{\cdot}TiO_2 + 6C + N_2 = 2Fe + 2TiN + 6CO(g) \tag{4}$$

A separate pellet consisting of a mixture of OSCOM grade rutile (TiO_2) and graphite was also prepared as per reaction (2). These pellets (around 10 mg) were loaded in an alumina crucible and heated under pure nitrogen flow up to 1400 °C at 5 °C/min, in a thermoanalyzer (model STA 409, Netzsch). Residual carbon analysis of the final products of carbonitrothermy was done by reheating the products in air up to 1000 °C, observing the weight gain as well as identifying the gas by Evolved Gas Analysis (EGA). Differential thermal curves (DTG) were drawn along with the weight gain (TG) curves which helped in the exact identification of the thermal events occurring in the process.

All the products from thermal analyzers and furnaces were crushed into fine powders in a tungsten carbide lined mortar pestle before being subjected to further characterization. Phase identification of the samples (around 2–3 mg) was carried out by X-ray diffraction (XRD) in an Inel-make unit (model MPD) with Cr-Kα radiation at 25 mA 35 kV using a curved position-sensitive detector. The elemental analysis of the same powders (sample weight of 500 mg) was done by EDXRF (energy dispersive-X ray fluorescence) analysis in air. The EDXRF analysis was done for detecting major elements (elements higher than sodium in periodic table) in the samples. For detection of trace elements, the samples were analyzed in inductively coupled plasma-atomic emission spectroscopy