Reducibility Study of Rossetta Ilmenite Ore Briquettes and Powder with Coke Breeze at 800-1100°C

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Abstract:
Ilmenite ore fine and coke breeze as reduced material were briquetted with different amounts of organic materials such as molasses or pitch were studied in this investigation. The produced briquettes at reasonable condition were reduced in nitrogen atmosphere at temperature range 800 - 1100°C to determine the factors controlling the reduction and to determine the controlling mechanism. Also ilmenite ore fine with coke breeze were reduced at the same temperature range in nitrogen atmosphere without briquetting process, for the sake of comparison.

Keywords: Ilmenite - reduction kinetic- briquetting- reduction by coke breeze.

1. Introduction

On heating ilmenite (FeTiO₃) with carbon in a stream of chlorine at 900°C, volatile TiCl₄ is obtained, the purified TiCl₄ is reduced by magnesium at 800°C in an atmosphere of argon and the silvery white metal is obtained [1].

Titanium is very hard, high melting and is stronger and much lighter than steal. It has better corrosion resistance than stainless steel. Its relative lightness combined with high mechanical strength makes it an excellent material, especially when alloyed with aluminum, for air craft construction. Titanium and its compounds have found uses in paints, electrical components, glass production and jewelry [2].

The reduction of synthetic ilmenite with graphite in the solid state was studied [3]. The reaction has been observed to initiate near 860°C at the contact points between the reactants. Up to 1020°C solid state reduction appears to be the main reaction mechanism, while above this temperature a rate increase has been observed and has been attributed to a change of mechanism to gaseous reduction of ilmenite by regenerated CO. Reduction rate data have been found to be well represented by the equation. 1 – 2x/3 – (1 –x)²/3 =K'. This equation is based upon diffusion of reactants through a product layer. CO is suggested as the diffusing species. The activation energy for the reaction in the temperature range 1075 to 1140°C has been calculated to be 64 ± 6 kcal per mole.

Some investigators [4] were found that when pellets prepared from mixtures of synthetic ilmenite and graphite and heated in argon at temperature range 1000 to 1100°C ,no
measurable reaction was obtained at 1000 °C but the rate was high at 1100 °C. An inflection in the reduction curve at about 2 pct weight loss at 1050 and 1100 °C was due to the difficulty in nucleating iron. The rate is increased significantly by the addition of ferric chloride which promotes the nucleation of iron. The addition of rutile decreases the rate of reduction and the addition of manganese stabilizes a pseudobrookite phase.

The effect of milling conditions on the low-temperature carbothermic reduction of the mineral ilmenite was studied [5], and it was found that after ball milling of an ilmenite-carbon mixture at room temperature, the ilmenite was reduced to rutile and metallic iron during subsequent low-temperature annealing (760°C for 30 minutes). A longer milling time results in a lower reduction temperature and a higher reduction rate. Higher milling intensity also leads to a lower reduction temperature. This enhanced reduction reaction induced by ball milling mainly results from the intimate mixing and large contact area between milled ilmenite and carbon particles.

The carbothermic reduction of Panzhihua ilmenite (FeTiO₃) [6] was studied at the temperature ranges from 900°C to 1400°C, and it was found that the reduction degree increases with increasing temperature. The reaction initiates at about 860°C. The reaction rate varies with temperature simultaneously. Impurities in Panzhihua ilmenite decrease the reduction degree. Magnesium and calcium oxide-rich zone is formed preventing complete reduction of Fe²⁺. In general, the reaction products are iron, TiO₂ and carbon.

The reduction of ilmenite concentrate with graphite under argon atmosphere between 1250°C and 1350°C was investigated [7]. Reduction of Fe³⁺ to Fe and Ti⁴⁺ to Ti³⁺ took place within 50% reduction during which a secondary oxide phase was formed and replaced the natural ilmenite. Reduction of Ti³⁺ to Ti²⁺ took place after 50% reduction which altered the composition of the secondary oxide phase by decreasing its oxygen content. Reduction of Ti²⁺ took place while the oxygen deficient TiO₁−ₓ phase formed. Formation of any titanium carbide or oxycarbide phases depended on the completion of the reduction which was not possible at the specified temperatures.

Some authors [8], used five models( unreacted core model for spherical particles of unchanging size, Ginstling model, Jander’s model, Prout-Tompkin model and Avarami model) for evaluation the controlling mechanisms of reduction of ilmenite with coal char in a rotary reactor. The results indicated that the rate controlling steps are solid-solid reaction during initial stages and diffusion of carbon monoxide through product layer during later stages of reaction. The activation energies for the two heterogeneous reactions are estimated to be 25 and 35 kcal/mol for solid-solid and gas-solid reactions, respectively. The experimental observation showing phase changes during reaction could not be confirmed either by Prout-Tompkin or Avarami models.

The reduction of Bama ilmenite concentrate containing 49.78% TiO₂ and 27.96% total Fe by graphite using thermogravimetric analysis system under argon atmosphere ambient from 850 to 1400°C was studied by some authors [9], and they found that the reduction degree of Bama ilmenite is enhanced with increasing temperature and the molar ratio of carbon to oxygen, and the reaction rate varies with temperature and reduction time simultaneously. The high content of impurities in Bama ilmenite evidently hastes the reduction of ilmenite. Forming the enrichment zone of manganese prevents complete reduction of Fe²⁺. The reduction products are mostly reduced iron, rutile, reduced rutiles, Ti₃O₅ and pseudobrookite solid solution. The reduction kinetics show that the reduction temperature is a key factor to control reaction rate.

The reduction of briquettes prepared mixtures of Rossetta ilmenite and coke breeze in nitrogen atmosphere from 800 – 1200°C was investigated [10]. The results indicated that, the reduction degree of the ilmenite increased with increasing stoichiometric ratio of carbon which, required converting all FeO & Fe₂O₃ to Fe and TiO₂ to Ti₃O₅. The reduction degree of the briquettes increased with temperature rise. The sample reduced at 1200 °C illustrated that the product contain α Fe and Ti₃O₅, rutile (TiO₂) and Pseudobrookite. At 800 °C the products
formed were ilmenite, rutile, anatase and traces of hematite

Briquetting process has several industrial benefits, mostly in indirect saving of energy and decreasing the environmental pollution. Taking in consideration that the produced briquettes go through a number of handling and transportation operations until they reach the metallurgical furnaces, so, the briquettes should have a sufficient strength to withstand all such external forces. Under room temperature the strength of briquettes and their properties are affected by many parameters as briquetting forces (briquetting load), compression time and particle size distribution of the raw materials. The optimum values of these parameters are inter-related and also depend on the composition of the briquettes [11]. To produce briquettes of satisfactory quality, it is necessary to use a binder for holding the particles together. There are different types of binders, such as lignin liquor, starch, petroleum bitumen, molasses, tar, asphalt, sulphur liquor, plastics, clay, sodium silicate, lime, bentonite and cement [12 - 15].

The present work aims to compare between the utility of two types of binding material (molasses and pitch) of the briquetting of ilmenite ore concentrate as well as establish the kinetic reduction of Rosetta ilmenite concentrate by coke breeze.

2. Materials and Experimental

2.1. Materials

Ore Characterization

A representative sample of Rosetta beach ilmenite concentrate was provided by the black sands project of Nuclear Material Authority (NMA) used for all experiments during this work. The compositions of Rosetta ilmenite ore concentrate contains about 43.6% TiO₂, 27.5% FeO and 20.9% Fe₂O₃.

The screen analysis of Rosetta ilmenite ore used in this investigation were nearly 65.5% in the fraction size -0.125 + 0.063 mm and 35% of given ore in fraction size - 0.25+0.125 mm.

X-ray diffraction analysis of Rosetta ore concentrate is shown in Fig. 1 From which it is clear that the components of Rosetta ilmenite concentrate are ilmenite FeTiO₃, pseudorutile Fe₂Ti₃O₉, hematite Fe₂O₃ and small quantity of rutile.

![Fig. 1. XRD analysis of Rosetta ilmenite ore concentrate.](image-url)
Coke breeze

The chemical composition of coke breeze used contain 90.6 % fixed carbon, 1.16% volatile matter, 8.24% ash, and 0.75% humidity. About 96.5% of the coke breeze fines used in this work have size in range -0.25+0.125 mm.

2.2. Experimental Procedures

Preparation of Samples

Preparation of Samples for the briquetting process was carried out by mixing of ilmenite ore concentrate with 1.5 stoichiometric ratio of carbon to convert all FeO & Fe₂O₃ to Fe and TiO₂ to Ti₃O₅ according to:

\[
\begin{align*}
\text{FeO} + C & \rightarrow \text{Fe} + \text{CO} \\
\text{Fe}_2\text{O}_3 + 3C & \rightarrow 2\text{Fe} + 3\text{CO} \\
3 \text{TiO}_2 + C & \rightarrow \text{Ti}_3\text{O}_5 + \text{CO}
\end{align*}
\]

10 grams of the mixture of ilmenite with 1.5 stoichiometric coke breeze with different amount of binder was pressed in the mould (12 mm diameter and a height 22 mm using MEGA.KSC-10 hydraulic press.

\[
\text{X} \times 100
\]

The stoichiometric amount of coke \( (Z) = \frac{X \times 100}{Y} \)

Where \( X \) = stoichiometric amount of carbon. \( Y \) = Percentage of carbon in coke.

The produced briquettes were subjected to mechanical tests (Drop damage resistance test) [16 - 18] and compressive strength tests (Annual Book of ASTM Standards).

Reduction Procedures

The reduction of ilmenite ore with carbon were done on thermogravimetric apparatus in nitrogen atmosphere (A schematic diagram of thermo gravimetric apparatus is shown in Fig. 2). It consists of a vertical furnace, electronic balance for monitoring the weight change of reacting sample and temperature controller. The sample was placed in an Alumina crucible which was suspended under the electronic balance by Ni-Cr wire. The furnace temperature was raised to the required temperature and maintained constant to ± 5 °C. Then sample was placed in the hot zone. The weight of the sample was continuously recorded at the end of the run; the sample was withdrawn from the furnace and kept in the desiccators.

Fig. 2. Schematic diagram of the apparatus.
The percentage of reduction was calculated according to the following equations:-

\[
\text{Percent of reduction} = \left( \frac{W_i - W_o}{W_i} \right) \times 100
\]

Where, \( W_o \), the initial mass of sample after removal of moisture. \( W_i \), mass of sample after each time, \( t \).

Oxygen (mass) indicates the mass of oxygen percent in ilmenite ore concentrate in form FeO & Fe_2O_3 and oxygen loss due to the conversion TiO_2 to Ti_3O_5.

3. Results and Discussions

Factors affecting on quality of the briquettes ilmenite concentrate of binding material

A. Effect of the percentage of binding material on the quality of the briquettes.

Fig. 3 Shows the effect of percentage of molasses or pitch on the drop number (drop damage resistance) and cold crushing strength of the briquette (the pressing load is constant = 294.3 MPa.). It is clear that as the percentage of binding materials increases both the drop damage resistance and crushing strength increased this due to the effect of binding material. Also from the same Fig.s it is clear that the use of pitch gave high value of both drop damage resistance and cold crushing strength .This fact may be due to the properties of the pitch being more viscous and considered as more binding materials.

B. Effect of the pressure load with constant amount of binding material on the quality of the briquettes.

Figs 4 shows the relation between the change of pressure load at constant amount of molasses or pitch (1.5%) on the drop number (drop damage resistance) and cold crushing strength of the briquette It is clear that as the pressing pressure load increased both the drop damage resistance and crushing strength increased .This may be due to the fact that increase pressure load increases the compaction of briquette and subsequently the Vander Waals forces increased [19 -20], also the increase of briquetting pressure leads to progressive crushing of the macro pores [21].
Fig. 4. Effects of Pressing on: (A) the drop damage resistance of the brick, (B) the compressive strength of the brick on using different organic binders (Percentage of organic binder = 1.5).

B. Effects of temperature on the reduction degree of ilmenite with coke breeze.

Experiments were performed in the temperature range of 800 to 1100ºC in nitrogen atmosphere. Plots of the reduction percentage of ilmenite by coke breeze as a function of time are shown in Fig.s 5-6. From these Fig.s, it is clear that the reduction rates increased with increasing temperature. At high reduction temperatures (more than 950 and up to 1100ºC), with increasing temperature, the oxygen removal increased. Also it is clear that the reduction of ilmenite ore with coke breeze in the form briquette (Figs.5) is more than the reduction of ilmenite with coke without briquetting (Fig. 6).

Fig. 5. Effects of temperature on the degree of reduction of the briquette of ilmenite with coke breeze where; (A) Molasses used as binder, (B) Pitch used as binder under pressing load = 294.3 MPa.
Fig. 6. Effects of temperature on the degree of reduction of the ilmenite with coke breeze mixture without briquetting.

**Kinetics of Reduction of Ilmenite Ore**

Applied model of solid reaction on the reduction of ilmenite ore concentrate with coke breeze [22].

\[ [1-(1-R)^{1/3}]^2 = kt \]

Where R is fractional reduction

\[ t \] is time and \( k \) is rate constant.

The results showed that this model gave straight line for all temperatures as shown in Figs. 7-8. The slopes of these straight lines gave the constant rate for each reduction temperature.

The logarithms (ln) of these constants were used to calculate the activation energies (Figs. 10-12). From the slopes of these straight lines, it was found that the activation energy of these reactions \( \approx 123 \) and \( 136 \) kJ/mole (Fig. 9), for reduction of ilmenite with coke breeze in the form of briquettes with molasses and pitch respectively. The activation energy for non briquettes \( \approx 110 \) kJ/mole, for reduction time \( \leq 45 \) min. at 1100ºC, (where jander equation will be applicable as in Fig. 10). These values correspond to solid diffusion control.

**Fig. 7.** Relationship between \([1-(1-R)^{1/3}]^2\) and reduction time of briquette of ilmenite with coke breeze where; (A) Molasses used as binder, (B) Pitch used as binder under pressing load = 294.3 MPa.
Fig. 8. Relationship between \([1-(1-R)^{1/3}]^2\) and reduction time of ilmenite with coke breeze without briquetting.

Fig. 9. Relationship between \(\ln k\) and \(1/T\); where (A) Molasses used as binder, (B) Pitch used as binder under pressing load = 294.3 MPa.

Fig. 10. Relationship between \(\ln k\) and \(1/T\) of ilmenite without briquetting.
4. Conclusions

1. The use of pitch gave high value of both drop damage resistance and cold crushing strength for the briquette of ilmenite and coke breeze.
2. As the pressing pressure load increased both the drop damage resistance and crushing strength of the briquette of ilmenite and coke breeze increased.
3. The reduction rates increased with increasing temperature. At high reduction temperatures (more than 950 and up to 1100°C), with increasing temperature, the oxygen removal increased. Also it is clear that the reduction of ilmenite ore with coke breeze in the form briquette is more than the reduction of ilmenite with coke breeze without briquetting.
4. The activation energy of this reaction \( \approx 123 \) and \( 136 \) kJ/mole for reduction of ilmenite with coke breeze in the form of briquettes with molasses and pitch respectively.

5. References


Садржај: У овом раду је проучавано брикетирање фине руде илменита и кокса као редукционог материјала са додатком различитих количина органским материјалом као што је молас. Брикети су редуковани у атмосфери азота у температурском интервалу од 800 - 1100°C ради одређивања фактора и механизма контроле редукције. Фина руда илменита са коксом је редукована у атмосфери азота у истом температурском интервалу без брикетирања, ради поређења резултата.

Кључне речи: илменит, кинетика редукције, брикетирање, редукција коксом