Briquetting of Egyptian Ilmenite Ore with Different Organic Binder and Reduced its in Hydrogen in Temperature Range 800 – 1200°C

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Abstract:
Ilmenite ore fine was briquetted with different amounts of molasses or pitch pressed under different pressure was studied in this investigation. The results show at optimum amount of molasses added was 1.5 % and pitch, the pressure was 294.3 M.Pa.. Also the characterizations of raw materials were studied by different methods of analyses such as X-ray and screen analyses. The produced briquettes were reduced by different amounts of hydrogen at different temperatures, and the reduction kinetics was determined.
Keywords: Ilmenite – reduction kinetic, Briquetting, Reduction by hydrogen.

1. Introduction
The demand of titanium is increasing in aerospace and commercial application [1]. The ilmenite ore is the main source for the production of metallic titanium and titanium dioxide [2].
The reduction of ilmenite concentrate is an important step in the titanium industry in order to decrease the reagent consumption and the waste material accumulation in the subsequent pigment making process [3]. Reduction of ilmenite with hydrogen is of current interest; both as the basis of environmentally begin metallurgical processes for producing high titania feedstock's that can be used in titania pigment production and as a possible means of supplying water or oxygen at future lunar bases [4].

Shomate et al [5], found from thermodynamic examination of reduction of of ilmenite was far less readily reduced than iron oxide by itself and he concluded that carbon was a better reducer of ilmenite than either hydrogen or carbon monoxide. Nicholson et al [6] describes an ilmenite upgrading route involving hydrogen reduction of ilmenite under pressure to give titanium dioxide and metallic iron, according to the following reaction;

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FeTiO₃ (solid) + H₂ → Fe (solid metal) + TiO₂ (solid) + H₂O (vapor)

Some investigators [7-11] published information concerned with the reduction of ilmenite with carbon dioxide and there is general agreement that reduction is more rapid in hydrogen than in carbon monoxide.

It was found that when cement ilmenite pellets was reduced by hydrogen at 1073 to 1273 K diffusion of gaseous species through product layer and intrinsic chemical reaction were found to be the main rate controlling factors during reduction [12].

Zhao and Shadman [13] found that when synthetic ilmenite reduced by hydrogen at temperature below 876°C the temporal profiles of conversion have a sigmoidal shape and indicate the presence of three different stages (induction, acceleration and deceleration) during reduction reaction. The apparent activation energy for the reaction is 22.3 kcal/mol whereas the intrinsic activation energy is 16.9 kcal/mol. And they indicated that TiO₂ can reduce to lower oxides of titanium at temperature higher than 876°C.

De Vries and Grey [14] found that when poly-granular synthetic ilmenite discs reduced by hydrogen at temperatures in the range 823 to 1173 K and at pressures in the range 1.2 to 13 atm., operation was achieved at high gas flow rates where gas film transport effects were negligible. Also they found that the reduction reaction proceeded topochemically and a shrinking core reaction model was found to be appropriate to predict conversion-time relationships and also they observed reduction rate increased sharply with pressure up to approximately 3 atm and then approached a plateau with further pressure increase.

During the utilization and transportation of ore to metallurgical furnaces as a powder, it loses a lot of fines and causes several environmental problems. So briquetting is an important process which is used to recycle and utilize the low grade ilmenite ore or ilmenite concentrate as a product with appropriate size and shape that will be a suitable feed for metallurgical furnaces. 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 it 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 up on the composition of the briquettes [15]. 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 [16-19]. The present work aims to comparison between the used of two type of binding material (molasses or pitch) of the briquetting of ilmenite ore concentrate as well as establish the kinetic reduction of Rosetta ilmenite concentrate by hydrogen.

2. Experimental Work

2.1 Raw Materials

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 X- ray analysis of Rosetta ore concentrate (Fig. 1) indicated that the components of Rosetta ilmenite concentrate are ilmenite FeTiO₃, pseudorutile Fe₃Ti₃O₉, hematite Fe₂O₃ and small quantity of rutile [20].

The chemical compositions of Rosetta ilmenite concentrate are presented in Tab. I. The screen analysis of Rosetta ilmenite ore (Tab. II) showed that nearly 65.5% in the fraction size -0.125+0.063 mm and 35% of given ore in -0.25+0.125 mm.
Fig. 1. XRD analysis of Rosetta ilmenite ore concentrate. (Hussiny and Shalabi [24])

Tab. I The chemical composition of Rosetta ilmenite ore.

<table>
<thead>
<tr>
<th>Components</th>
<th>Percentage, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>43.6</td>
</tr>
<tr>
<td>FeO</td>
<td>27.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>20.6</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.48</td>
</tr>
<tr>
<td>MnO</td>
<td>1.15</td>
</tr>
<tr>
<td>MgO</td>
<td>0.4</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.17</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.06</td>
</tr>
<tr>
<td>S</td>
<td>0.025</td>
</tr>
<tr>
<td>C</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Tab. II The screen analysis of Rosetta ilmenite ore.

<table>
<thead>
<tr>
<th>Size Fraction, mm</th>
<th>Percentage, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 0.25 + 0.125 mm</td>
<td>34.23</td>
</tr>
<tr>
<td>- 0.125 + 0.063 mm</td>
<td>65.47</td>
</tr>
</tbody>
</table>

2.2. Reduction Procedures

The reduction of ilmenite ore by hydrogen were done on thermo gravimetric apparatus (A schematic diagram of thermo gravimetric apparatus is shown in Fig. 2 It consisted 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 (800-1150 °C) and maintained constant to ± 5 °C. Then samples were placed in hot zone.

The nitrogen flow rate was 0.5 l/min on all the experiments. at initial time and after the end of reduction only. The weight of the sample was continuously recorded. At the end of the run, the samples were withdrawn from the furnace and putted in the desiccators.

The percentage of reduction was calculated according to the following equations:
Percent of reduction = \( \frac{(W_0 - W_t) \times 100}{\text{Oxygen (mass)}} \)

Where \( W_0 \) the initial mass of sample after removal of moisture.

\( W_t \) mass of sample after each time, t.

Oxygen (mass) indicates the mass of oxygen percent in ilmenite ore concentrate in form \( \text{FeO} \) and \( \text{Fe}_2\text{O}_3 \) and oxygen loss due to convert \( \text{TiO}_2 \) to \( \text{Ti}_3\text{O}_5 \).

3. Results and discussion

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

Figs. 3. and 4. 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 increase both the drop damage resistance and crushing strength increased this due to the effect of binding material.

Also from the same Figs. 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 pitch more viscous and more binding materials.
3.2. Effect of the pressure load with constant amount of binding material on the quality of the briquettes

Figs. 5 and 6 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 increase the compaction of briquette and subsequently the Vander Waals forces increased [21-22], also this may be due to the increase of briquetting pressure leads to progressive crushing of the macropores [23]
3.3. Effect of hydrogen flow rate on the reduction degree

Fig. 7 illustrate the relation between the reduction degree and hydrogen flow rate when the reduction were done at constant temperature (900°C) and constant weight of the sample. It is clear that as the flow rate of hydrogen increased the reduction percentage increased. This may be the increase of flow rate leads to an increase of number of hydrogen mole in the bulk phase, which in turn leads to the raise of hydrogen adsorption and subsequently the rate of reaction increased [24] or the increase of flow rate increased the gas diffusion across the boundary layer subsequently the reduction ion increased [25,26]. Also may be the higher flow rate prevailing in the reaction zone which enhances the rate of hydrogen absorption and subsequently the rate of chemical reaction steps increased [27,28].

![Fig. 7. Effect of flow rate on the reduction percentage (Temperature of reduction was 900 °C & time of reduction was 60 min.).](image)

3.4. Effect of the reduction temperature on the reduction degree

The reduction was carried out at different temperatures ranging from 800 to 1100°C, where the weight of the briquette were constant and the hydrogen flow rate =1.5 liter/min. The results of the investigation are shown in Fig. 8 for the briquette binding by molasses and Fig. 9 for the briquette binding with pitch.

![Fig. 8. Effect of reduction time on the percent of reduction by hydrogen of briquettes (ilmenite concentrate + 1.5 % molasses) pressed at 294.3 MPa at different temperatures.](image)
Fig. 9. Effect of reduction time on the percent of reduction by hydrogen of briquettes (ilmenite concentrate + 1.5 % pitch) pressed at 294.3 MPa at different temperatures.

It is clear that the increase of temperature favors the reduction rate and degree. At high reduction temperature, with increasing temperature, the oxygen removal increased. Also it is clear that the reduction of the briquette binding by pitch is less than the briquette binding by molasses this may be due to the binding by molasses gave briquette have more pore than in case of binding by pitch. The analyses of the curves relating the reduction percentage and time of reduction, shows that each curve has 3 different slopes indicating 3 different values of reduction rates. The first value is high, while the second is somewhat slower and the third is slowest one. The increase of reduction percentage with rise of temperature may be due to the increase of number of reacting moles having excess of energy which leads to the increase of reduction rate [24,29]. Also the raise of temperature leads to an increase of the rate of mass transfer of the diffusion and rat of desorption [26,28,30].

3.5. Kinetics reduction of ilmenite briquette

Using diffusion process controls equation (Yuming Wang and Zhangfu Yuan [1]

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

Where \(x\) is fractional reduction, \(t\) is time of reduction, \(k\) is the rate constant.

Fig.10 and Fig.11 illustrate the relation between 1-\((2/3) X - (1-X)^{2/3}\) against time of reduction for different reduction temperature. From which it is clear that the straight line was observed.

Fig. 10. The relationship between time of reduction and 1-0.666X- (1-X)*0.666 at different temperature (molasses).
Fig. 11. The relationship between time of reduction and $1-0.666X - (1-X)*0.666$ at different temperature (pitch).

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction. The results illustrate in Figs. 12 and 13, from which it is clear that the activation energy = 76.72 kJ/mole for briquette binding by molasses (Fig.12), while the activation energy = 99.64 kJ/mole for the briquette binding with pitch (Fig.13).

These results indicate that the reduction of the briquette with molasses is easily reduction than case using pitch as a binder material.

Fig. 12. The relation between $1/T$ and $\ln K$ for molasses using as a binder. (Arrhenius plot for reduction reaction)

Fig. 13. The relation between $1/T$ and $\ln K$ for pitch using as a binder. (Arrhenius plot for reduction reaction)
3. 6. X-Ray analyses of the reduced briquette A-X-ray analyses of the reduced sample (used molasses as a binder)

A-1-It is clear that the phases of the sample after reduction at 800°C (time of reduction 90 min.) (Fig.14) (in case of molasses used as a binder) are ilmenite, metallic iron, rutile and some traces of magnetite, this indicate that the reduction is not completed and this clear from the reduction curve (the reduction percentage is about 50%). The reaction at 800°C may be carried out as follows:
1-Pseudrutile is reduced directly to ilmenite and rutile according to this reaction
   \[ \text{Fe}_2\text{Ti}_3\text{O}_9 + \text{H}_2 \rightarrow 2 \text{FeTiO}_3 + \text{TiO}_2 + \text{H}_2\text{O} \]
2-Then part of ilmenite reduced by hydrogen to rutile and metallic iron according to the following reaction
   \[ \text{FeTiO}_3 + \text{H}_2 \rightarrow \text{Fe} + \text{TiO}_2 + \text{H}_2\text{O} \]
3-Part of hematite reduced to magnetite then some of magnetite reduced to the iron, thus some traces of magnetite were present in x-ray.

A-2- X-ray of the sample reduced at 1000 oC (in case of molasses used as a binder) shows the phases present are metallic iron, rutile, some traces of magnetite and pseudobrookite (this indicate that the reduction is not completed. The reaction at 1000°C may be carried out as follows:
1-Pseudrutile decomposed to pseudobrookite and rutile because the sample held for some time at that temperature in nitrogen atmosphere before the reluctant is admitted.
   \[ \text{Fe}_2\text{Ti}_3\text{O}_9 \rightarrow \text{Fe}_2\text{TiO}_5 + 2 \text{TiO}_2 \]
2- Then ilmenite is reformed by a recombination reduction process according to the following reaction
   \[ \text{Fe}_2\text{TiO}_5 + \text{TiO}_2 + \text{H}_2 \rightarrow 2 \text{FeTiO}_3 + \text{H}_2\text{O} \]
2-Then ilmenite reduced by hydrogen to rutile and metallic iron according to the following reaction
   \[ \text{FeTiO}_3 + \text{H}_2 = \text{Fe} + \text{TiO}_2 + \text{H}_2\text{O} \]

B- X-ray analyses of the reduced sample (used pitch as a binder).

B-1-It is clear that the phases of the sample after reduction at 800°C (time of reduction 65 min.) (Fig.15) are ilmenite, metallic iron, rutile and some traces of magnetite, this indicates that the reduction is not completed and this clear from the reduction curve (time of reduction 65min. The reaction at 800°C may be carried out as follows:
1-Pseudrutile is reduced directly to ilmenite and rutile according to this reaction
   \[ \text{Fe}_2\text{Ti}_3\text{O}_9 + \text{H}_2 \rightarrow 2 \text{FeTiO}_3 + \text{TiO}_2 + \text{H}_2\text{O} \]
2-Then part of ilmenite reduced by hydrogen to rutile and metallic iron according to the following reaction
   \[ \text{FeTiO}_3 + \text{H}_2 = \text{Fe} + \text{TiO}_2 + \text{H}_2\text{O} \]
3-Hematite reduced to magnetite then of magnetite reduced to the iron.

B-2. X-ray of the sample reduced at 1100°C (time of reduction 65 min) shows the phases present are metallic iron, pseudobrookite solid solution \( \text{Fe}_3\text{Ti}_3\text{O}_{10} \) and small amount of anatize (\( \text{TiO}_2 \)) as show in Fig.14. The formation of the pseudobrookite solid solution may be formed before the reluctant is admitted or may be formed by the following reaction
   \[ \text{Fe}_2\text{TiO}_5 + 2\text{TiO}_2 + \text{FeO} \rightarrow \text{Fe}_3\text{Ti}_3\text{O}_{10} \]
Fig. 14. XRD analysis of the reduced briquette of Rosetta ilmenite ore concentrate (used molasses as a binder).

Fig. 15. XRD analysis of reduced briquette of Rosetta ilmenite ore concentrate (used pitch as a binder).

4. Conclusions

1. The crushing strength and the drop damage resistances used as the amount of binder increases, and it is higher when used pitch than the case used molasses.
2. The reduction rates increased with increasing temperature of the reduction.
3. The reduction rate increased of hydrogen flow rate at constant temperature of reduction.
4. The reduction degree is higher in case of the used molasses as binder material than in case of pitch.
5. The diffusion process through the product layer is the reduction control step.
6. The activation energy of the reduction depend on the binding used, for molasses as binder energy of activation = 76.72 kJ/mole, while for pitch as binder the activation energy = 99.64 kJ/mole.
7. The phase's product after reduction depends upon the temperature of reduction and type of binder used.

5. References

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Садржај: Фина руда изменит са различитим садржајем моласе или другог органског једињења је брикетирана под различитим притисцима. Резултати су показали да је оптимални садржај додате моласе 1,5% и притисак од 294,3 MPa. Такође, карактеризација материјала је урађена различитим методама као што су рентгенска дифракција и скенирајући анализе. Брикети су редуковани различитим количинама водоника под различитим температурама и одређена је кинетика редукције.

Кључне речи: изменит – кинетика редукције, брикетирање, редукција водоником