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BRIQUETTING OF ROSETTA ILMENITE ORE WITH DIFFERENT ORGANIC BINDER AND ITS REDUCTION IN HYDROGEN IN THE TEMPERATURE RANGE OF 800÷1200°C

1. Introduction

The demand for titanium is increasing in aerospace and commercial applications [29]. Also the demand for titanium dioxide, which was used in paper, plastics and pigment industries is increased. The ilmenite ore is the main source for the production of metallic titanium and titanium dioxide [14].

The reduction of ilmenite concentrate is an important problem in the titanium industry in order to decrease the reagent consumption and the waste material accumulation in the subsequent pigment production process [20]. Reduction of ilmenite with hydrogen is the topic of current interest; both as the basis of environmentally benign metallurgical processes for producing high titanium feedstock that can be used in titanium pigment production, as well as possible means of supplying water or oxygen at future lunar bases [4, 31].

Schomate *et al.* [24], found from thermodynamic examination of reduction of ilmenite that it was far less readily reduced than iron oxide by itself and they concluded that carbon was a better reducer of ilmenite than either hydrogen or carbon monoxide.

Nicholson *et al.* [19] describe an ilmenite upgrading route involving hydrogen reduction of ilmenite under pressure to produce titanium dioxide and metallic iron, according to the following reaction.

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Donelly *et al.* [5, 7, 8, 12, 28] 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.

Kang Sun, Reijiro Takahashi and Jun-ichiro Yagi [13] 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.

Briggs and Sacco indicated that the removal of oxygen from ilmenite disks occurs in temperature between 823 and 1353°K. Under a hydrogen atmosphere, a shrinking core reduction model, modified to include the growth of this iron film, was capable of predicting the conversion-time relationships of ilmenite samples. Activation energy of 43.2 ±2.6 kcal/mole was determined to be representative of reaction control over the temperature range 823÷1023°K.

Zhao and Shadman [30] found that when synthetic ilmenite was 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. Furthermore, they indicated that TiO₂ can be reduced to lower oxides of titanium at temperature higher than 876°C.

Kapilashrami found that the reduction proceeds very fast in the initial period and a high degree of reduction is obtained in the case of all reductions and a decrease in the reaction rate is observed at later stages of the reduction due to the slow diffusion process. Activation energy for the reduction of FeTiO₃ to iron and titanium dioxide was estimated to be of 108 kJ.mole⁻¹.

De Vries and Grey [4] 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., stable 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 sharp increasing of reduction rate with pressure up to approximately 3 atm. Then it 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

they reach the metallurgical furnaces, 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 [16]. 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 [2, 3, 15, 27,]. The present work aims to compare between the two types of used binding material (molasses or pitch) for the briquetting of ilmenite ore concentrate as well to establish the kinetics reduction of Rosetta ilmenite concentrate by hydrogen.

2. Experimental work

2.1. Raw Materials

Raw material used in this work was Rosetta ilmenite ore concentrate. The x-ray of Rosetta ilmenite ore used in this experiments mainly concerned ilmenite FeTiO_3 , pseudorutile $\text{Fe}_2\text{Ti}_3\text{O}_9$, hematite Fe_2O_3 and small quantity of rutile (Fig. 1).

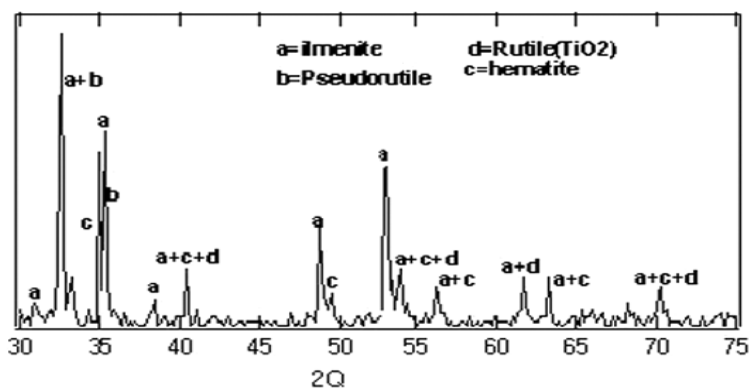


Fig. 1. XRD analysis of Rosetta ilmenite ore concentrate

The chemical compositions of Rosetta ilmenite concentrate are presented in Table 1. The screen analysis of Rosetta ilmenite ore (Tab. 2) showed that it consists of nearly 65.5% within the fraction size $-0.125 + 0.063$ mm and 34.2% of given ore within $0.25 + 0.125$ mm.

TABLE 1
The chemical composition of Rosetta ilmenite ore

Components	Percentage, %
TiO ₂	43.6
FeO	27.5
Fe ₂ O ₃	20.6
SiO ₂	1.48
MnO	1.15
MgO	0.4
V ₂ O ₅	0.17
Cr ₂ O ₃	0.06
S	0.025
C	0.35

TABLE 2
The screen analysis of Rosetta ilmenite ore

Size Fraction, mm	Percentage, %
-0.25 + 0.125	34.23
-0.125 + 0.063	65.47

2.2.1. Preparation of samples

Preparation of samples for the briquetting process was carried out by mixing of ilmenite ore concentrate with different amount of binder (molasses or pitch). The 10 grams of mixture of ilmenite with different amount of binder was pressed in the mould (12 mm diameter and a height 22 mm, using MEGA.KSC-10 hydraulic press).

The produced briquettes were subjected to mechanical tests (drop damage resistance test [9, 10, 17] and compressive strength tests [1]).

2.2.2. Reduction procedures

The reduction of ilmenite briquette by hydrogen was done on thermo gravimetric apparatus (a schematic diagram of thermo gravimetric apparatus is shown on Figure 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 aluminum 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 a 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 kept in the desiccators.

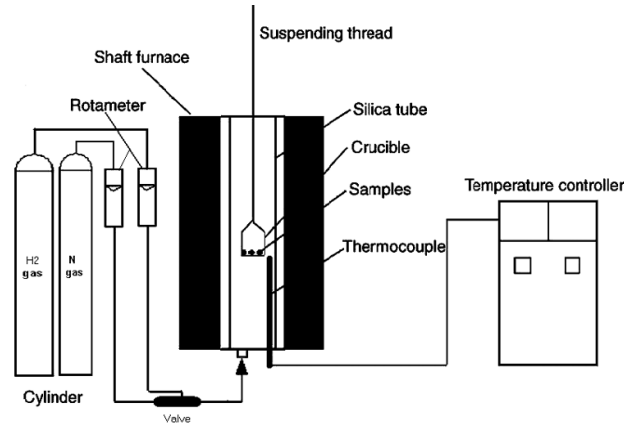


Fig. 2. Schematic diagram of the apparatus

The percentage of reduction was calculated according to the following equations:

$$\text{Percent of reduction} = \frac{(W_0 - W_t) \cdot 100 \cdot 16}{\text{Oxygen (mass)} \cdot 28} \quad (2)$$

where:

W_0 — is 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 FeO & Fe₂O₃ and oxygen loss due to convert TiO₂ to Ti₃O₅.

3. Results and discussion

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

Figures 3 and 4 show 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 due to the influence of binding material.

Also from the same figures it is clear that the use of pitch gave high value of both drop damage resistance and cold crushing strength. This fact may be caused by the fact that pitch is more viscous and more binding material.

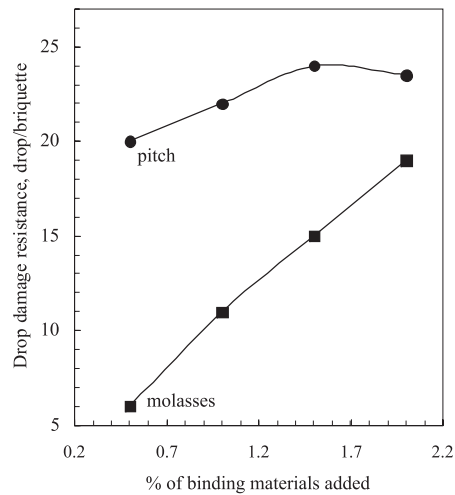


Fig. 3. Effect of change of binding materials addition on the drop damage resistance of produced briquette at constant pressure 294.3 MPa

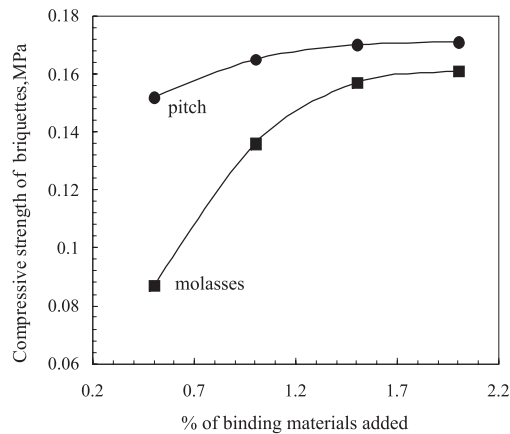


Fig. 4. Effect of change of binding materials addition on the compressive strength of produced briquette at constant pressure 294.3 MPa

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

Figures 5 and 6 show 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 force 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 van der Waals forces increased. Furthermore, the increase of briquetting pressure leads to progressive crushing of the macropores [11].

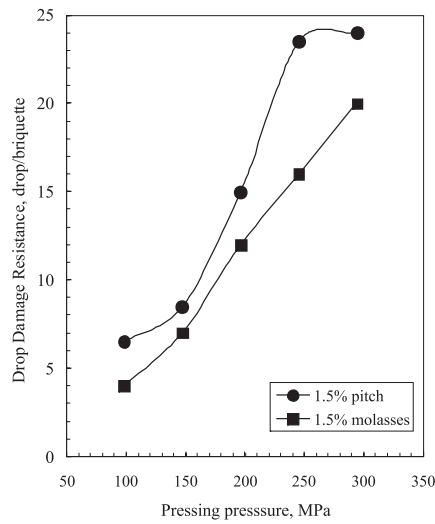


Fig. 5. Effect of pressing pressure on the drop damage resistance of produced briquettes at constant materials percent

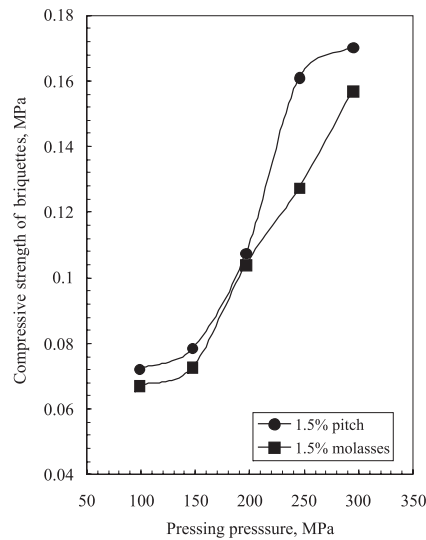


Fig. 6. Effect of pressing pressure on the compressive strength of produced briquettes at constant binding materials percent

3.2. Effect of hydrogen flow rate on the reduction degree

Figure 7 illustrates the relation between the reduction degree and hydrogen flow rate when the reduction were done at constant temperature (900°C) and the weight of the sample was constant. It is clear that as the flow rate of hydrogen increased the reduction percentage increased. This may be due to the fact that increase of flow rate leads to increasing of number of hydrogen moles in the bulk phase, which in turn leads to the raise of hydrogen adsorption. In this way, the rate of reaction increased [25] or the increase of flow rate increased and the gas diffusion across the boundary layer subsequently the ion reduction increased [18, 22]. 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 [21, 23].

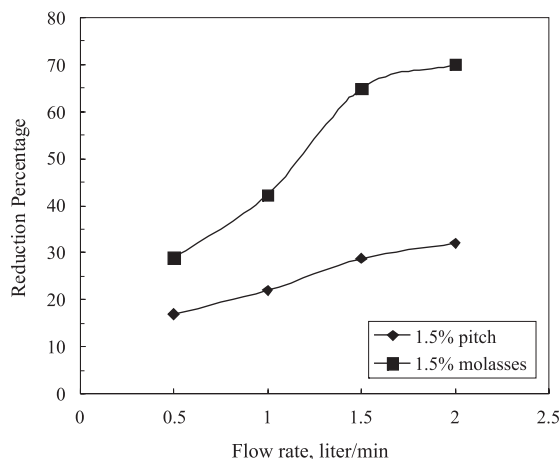


Fig. 7. Effect of flow rate on the reduction percentage (Temperature of reduction was 900°C & time of reduction was 60 min)

3.3. Effect of the reduction temperatue 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 on Figure 8 for the briquette binding with molasses and Figure 9 for the briquette binding with pitch.

It is clear that the increase of temperature favors the reduction rate. 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 occur due to the fact that binding by molasses gave briquette that is more porous than in case of binding by pitch. The analyzes of the curves relating the reduction percentage and time of reduction, show that each curve has 3 different slopes indicating

3 different values of reduction rates. The first value is high, while the second one is somewhat lower and the third is the lowest one. The increase of reduction percentage with rise of temperature may occur due to the increase of number of reacting moles having excess of energy what leads to the increase of reduction rate [25, 26]. Also the raise of temperature leads to an increase of the rate of mass transfer of the diffusion and rate of desorption [6, 23, 24, 26].

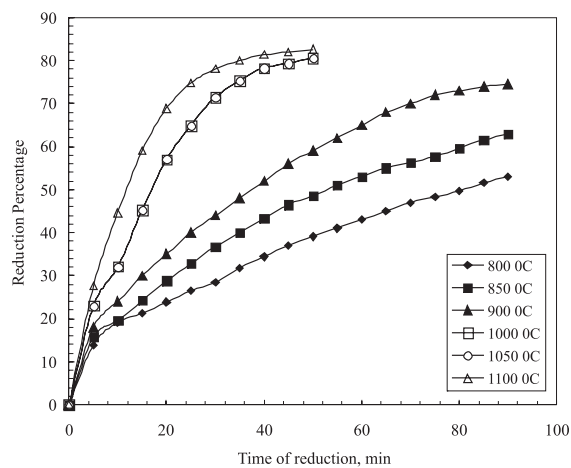


Fig. 8. Effect of reduction time on the percent of reduction by hydrogen of briquettes (ilmenite concentrate + 1.5% molasses) pressed at 294.3 MPa at different temperatures

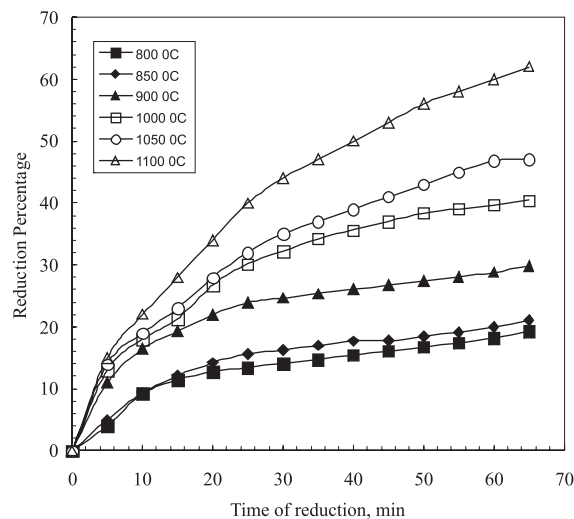


Fig. 9. Effect of reduction time on the percent of reduction by hydrogen of briquettes (ilmenite concentrate + 1.5% pitch) pressed at 294.3 MPa at different temperatures

3.4. Kinetics reduction of ilmenite briquette

Using diffusion process controls equation (29)

$$1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}} = kt \quad (3)$$

Where X is fractional reduction, t is time of reduction, k is the rate constant.

Figures 10 and 11 illustrate the relation between $1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}}$ against time of reduction for different reduction temperature. From which it is clear that the relationship is represented by straight line.

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction. The results were illustrated on Figures 12 and 13, from which it is clear that briquette binding by molasses have activation energy = 76.72 kJ/ mole (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 easier than in the case of using pitch as a binder material.

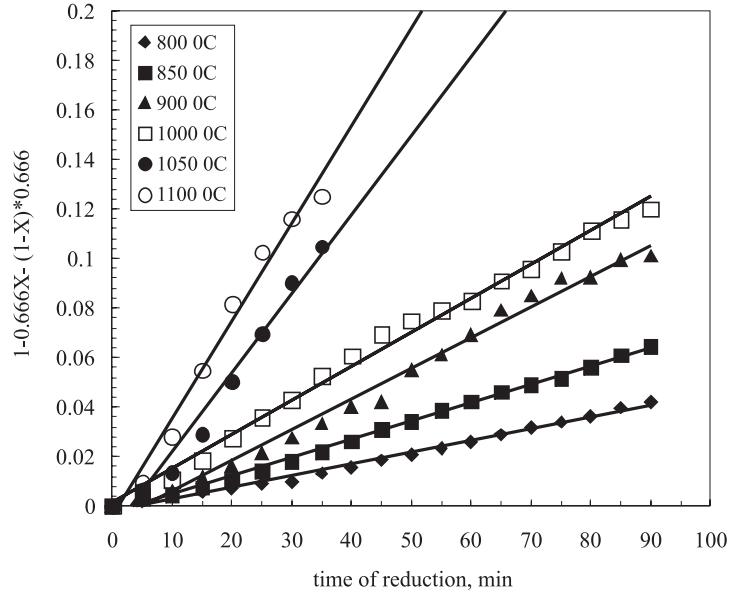


Fig. 10. The relationship between time of reduction and $1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}}$ at different temperature (molasses)

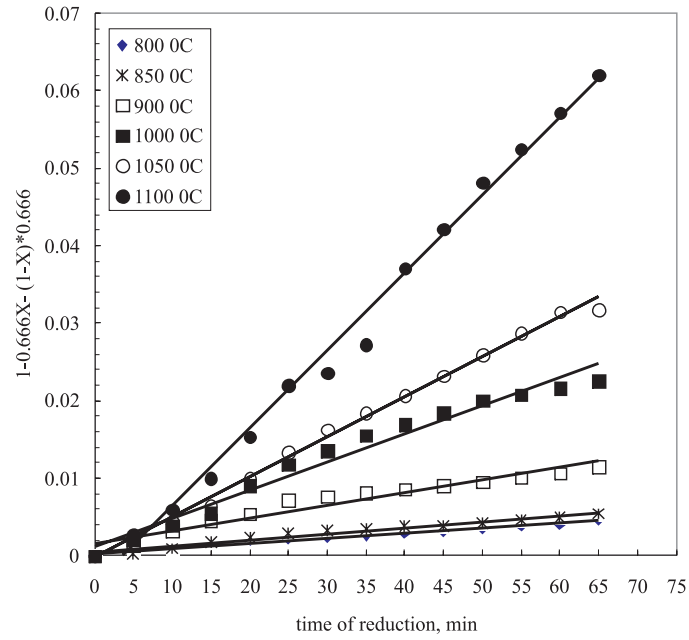


Fig. 11. The relationship between time of reduction and $1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}}$ at different temperature (pitch)

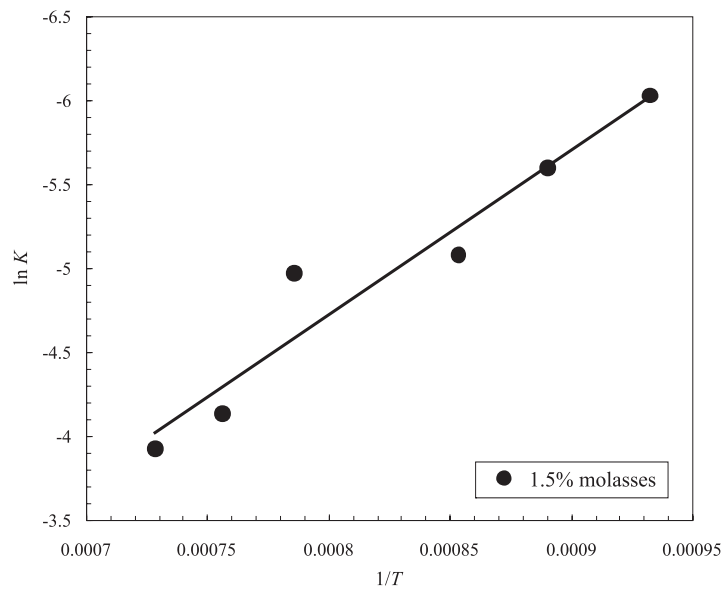


Fig. 12. The relation between $1/T$ and $\ln K$ for molasses using as a binder (Arrhenius plot for reduction reaction)

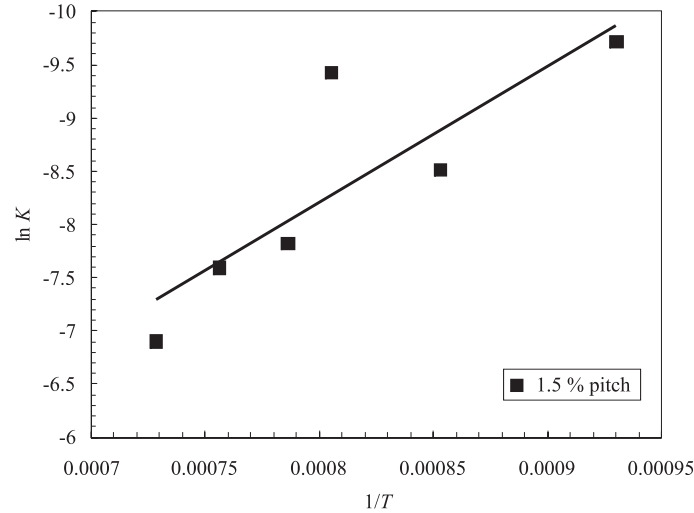


Fig. 13. The relation between $1/T$ and $\ln K$ for pitch using as a binder (Arrhenius plot for reduction reaction)

3.5. X-Ray analyses of the reduced briquette

X-ray analyzes of the reduced sample (used molasses as a binder)

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 indicates that the reduction is not completed and this is clear from the reduction curve (the reduction percentage is about 50%). The reaction at 800°C may be carried out as follows:

- 1) Pseudorutile is reduced directly to ilmenite and rutile according to this reaction.



- 2) Then part of ilmenite was reduced by hydrogen to rutile and metallic iron according to the following reaction.



- 3) Part of hematite was reduced to magnetite then some of magnetite reduced to the iron, thus some traces of magnetite were detected by x-ray analysis.

X-ray analyzes of the sample reduced at 1000°C (in Case of molasses used as a binder) shows that the present phases are metallic iron, rutile, some traces of magnetite and pseudobrookite (this indicates that the reduction is not completed).

The reaction at 1000°C may be carried out as follows:

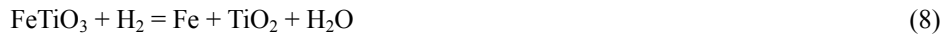
- 1) Pseudorutile decomposed to pseudobrookite and rutile because the sample held for some time at that temperature in nitrogen atmosphere before the reductant is admitted.



- 2) Next ilmenite is reformed by a recombination reduction process according to the following reaction.



- 3) Then ilmenite was reduced by hydrogen to rutile and metallic iron according to the following reaction.



X-ray analyzes of the sample reduced at 1000°C (In Case of molasses used as a binder) shows the phases present are metallic iron, pseudobrookite, rutile, some traces of magnetite the crystallinity of rutile is very weak.

X-ray analyses of the reduced sample (Used pitch as a binder)

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 is clearly visible from the reduction curve (time of reduction 65 min). The reaction at 800°C may be carried out as follows:

- 1) Pseudorutile is reduced directly to ilmenite and rutile according to this reaction.



- 2) Then part of ilmenite was reduced by hydrogen to rutile and metallic iron according to the following reaction.



- 3) Hematite was reduced to magnetite then magnetite reduced to the iron.

X-ray analyzes of the sample reduced at 1100°C (time of reduction 65 min) showed that the present phases are metallic iron, pseudobrookite solid solution $\text{Fe}_3\text{Ti}_3\text{O}_{10}$ and small amount of anatase (TiO_2) as is shown on Figure 14. The formation of the pseudobrookite solid solution may be formed before the reductant is admitted or may be formed by the following reaction:



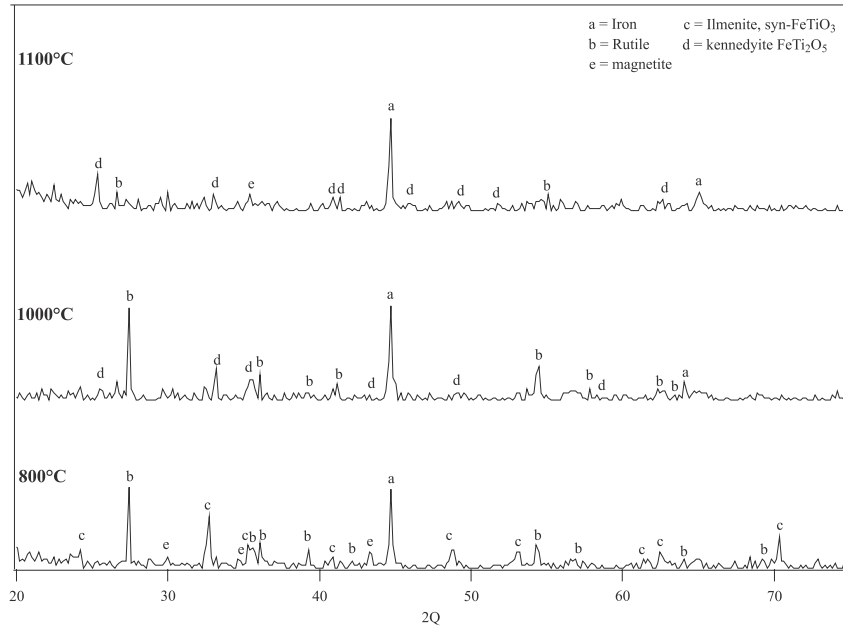


Fig. 14. XRD analysis of reduced briquette of Rosetta ilmenite ore concentrate (Used molasses as a binder)

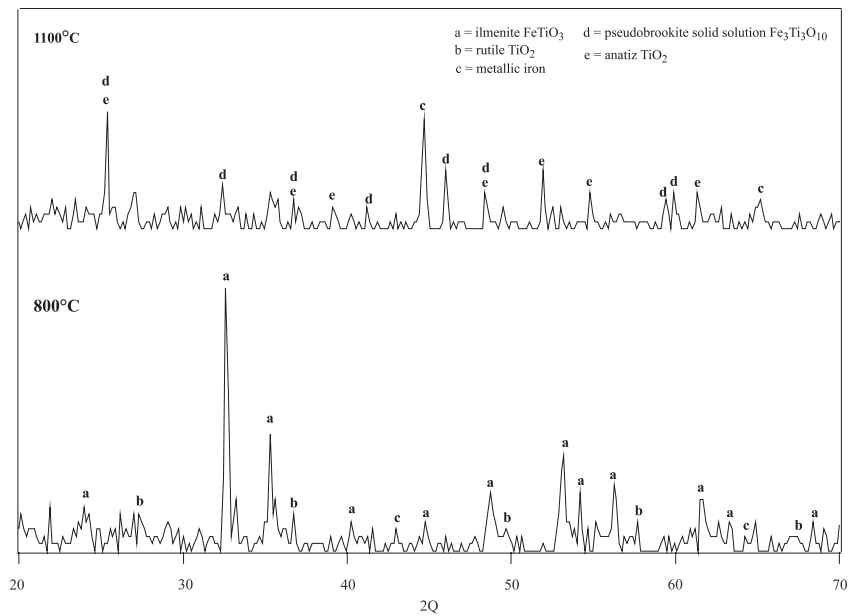


Fig. 15. XRD analysis of reduced briquette of Rosetta ilmenite ore concentrate (Used pitch as a binder)

4. Conclusions

- 1) The crushing strength and the drop damage resistances increased, and it is higher in case of pitch than in case of molasses.
- 2) The reduction rates increased with increasing temperature of the reduction.
- 3) The reduction rate of hydrogen flow rate at constant temperature of reduction increased.
- 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 depends on the type of applied binding, 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 on the temperature of reduction and type of used binder.

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