ISSN 2229-5518

Pelletization of Titanomagnetite Concentrate (TMC) and Its Reduction by Hydrogen in Static Beds.

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Abstract – Titanomagnetite concentrate pellets in this investigation were produced by using 2.5 % molasses as binder with 8.5 % water from the total weight of the charge and dried for 48 hours in room temperature. Reduction kinetics of titanomagetite concentrate TMC pellets produced from Rossetta – Ilmenite ore via 21/ min hydrogen flow rate were investigated at different temperatures ranging from 600 to 950 ^{o}C. It was found that the best reduction properties were found at 950 ^{o}C. The main crystalline phases of reduced pellets at 950 ^{o}C were metallic iron (syn. Fe), rutile (syn. TiO_2) and some traces of magnetite (Fe_3O_4).

Key words – Titanomagnetite, Ilmenite .Hydrogen, Reduction kinetics.

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1. INTRODUCTION

Vjay *et al*. [1] investigated the reduction of Quilon ilmenite beach sand with hydrogen in a fluidized bed reactor and found that the reduction period could be divided into three distinct stages: initial slow induction stage, intermediate acceleratory stage and final slowing down stage.

Park and Ostrovski [2] have shown that the reduction of New Zealand TTM iron-sand in the fixed bed reactor by hydrogen gas was slower than that of hematite or magnetite iron ores.

Wang *et al*. [3] studied the hydrogen reduction kinetics of Bama ilmenite and considered that diffusion of hydrogen gas in the reduced layer was the rate controlling step.

Dang *et al*. [4] have investigated the reduction of titanomagnetite powder containing 56.9 mass% of iron and 9.01 mass% of TiO2 with H_2-Ar gas mixtures in isothermal experiments using thermo-gravimetric analyzer (TGA). The reduction of titano-magnetite was proved to proceed via a dual reactions mechanism. The first reaction is reduction of titano-magnetite to wüstite and ilmenite and the second one is reduction of wüstite and ilmenite to iron and titanium-containing phase. It was found that the dual reactions occurred simultaneously during the reduction. The reduction kinetics of titano-magnetite was analyzed according to a dual reactions kinetic model and the results indicated that the gaseous species diffusion in product layer was the rate controlling step for the first reaction, and interfacial chemical reaction was that for the second reaction. The apparent activation energies were extracted to be 98 kJ/mol and 115 kJ/mol for the first and second reaction respectively.

Haoyan , et al [5] was reduced Titanomagnetite concentrate by H_2–Ar gas mixtures in a laboratory fixed bed reactor at the temperatures from 1123 to 1323 K. Results have shown that both the reduction and metallization degrees increased with the increase of temperature and hydrogen content. Due to the low iron oxides content and the high impurities content such as magnesium oxide that baffled the reduction of Fe^{2+} in TTM concentrate, the reduction degree of TTM concentrate is lower than that of TTM ironsand at the same reduction condition. Above 1123 K, the reduction is mainly controlled by interfacial chemical reaction in the whole reduction process and the reduction path is suggested as follows:

$Fe_{3-x}Ti_xO_4 \rightarrow (x+y-1)FeO + Fe_{4-2x-y}TixO_{4-y} \rightarrow (x+y-1)Fe + Fe_{4-2x-y}TixO_{4-y} \rightarrow (3-x)Fe + xTiO_2$ $(0<y<4-2x, x=0.27\pm0.02)$

Naglaa et al .[6] indicated that : 1- The reduction rates Titanomagnetite Concentrate Briquette Produced from Rossetta-Ilmenite via Hydrogen increased with increasing temperature of the reduction from 600˚C up to 950˚C.

2 - The reduction rate increased with the increase of hydrogen flow rate at constant temperature.

3 - The diffusion processes through the produced briquettes is the reduction control step and the have activation energy = 33.223 kJ/mole for model $1-2/3f-(1-f)^{(2/3)} = kt$, while the activation energy = 30.389 kJ/mole for model $1-3(1-f)^{2/3}+2(1-f) = kt$ respectively

The aim of this investigation is to obtain data on reduction behavior of titanomagnetite pellets that produced from the concentration process of Rossetta beach ilmenite ore which was provided by the black sands project of Nuclear Material Authority (NMA) via hydrogen gas at moderate temperature

2. EXPERIMENTAL WORK

2.1. Raw Materials

1-Centeral Metallurgical Research and Development Institute, (CMRDI). Cairo, Egypt.
2-Egyptian Iron and Steel Company, Helwan, Egypt.
3- King Khalid University, Faculty of science and Arts For Girls. Sarat Abida . Saudi Arabia.
4- Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt.
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The titanomagnetite concentrate (TMC) used in this study was obtained from Rossetta-Ilmenite ore that was supplied by Nuclear Materials Authority (NMA). The chemical composition of titanomagnetite concentrate is listed in Table 1.

Table 1. The chemical compositions of the titanomagnetite concentrate (TMC)

Components	Percentage, %.
Fe	52.71
FeO	23.22
SiO_2	4.3
CaO	1.05
MgO	1.17
Al_2O_3	1.72
MnO	0.56
S	0.04
P_2O_5	0.08
TiO_2	18.06

Phase characteristic of sample was investigated by XRD. X-ray diffraction (XRD, Bruker axs D8, Germany) with Cu-K (λ=1.5406 Å) radiation and secondary monochromator in the range 2θ from 20 to 75° was used to identify the formed phases. A Nikon Eclipse TS100 Optical Microscope (OM) with a Kodak Megaplus Camera in conjunction with Clemex Vision Professional Edition software was used for observation of the microstructure and image analysis.

The results of x-ray diffraction of the sample as shown in Figure 1, indicate that the main crystalline phases of concentrate are Ilmenite ($Fe^{+2}TiO_3$) Magnetite (Fe_3O_4), Hematite(Fe_2O_3)and traces of Anatase (TiO_2).

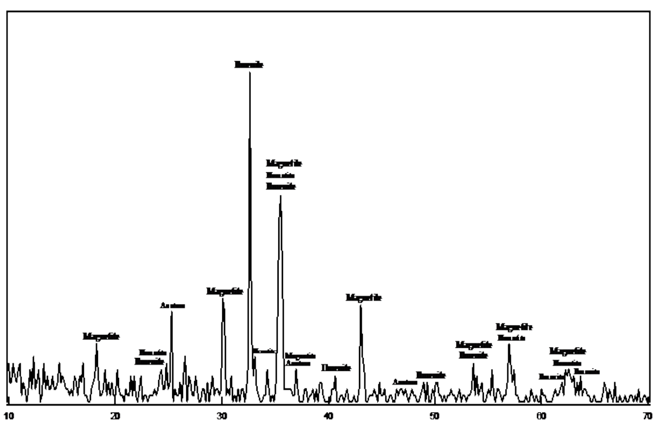

Fig. 1. XRD for original sample

2.2. Preparation of The Pellets and Its Physical Properties

TMC was grinded in vibrating mill to powder with size less than 75 micrometers. After which the pellitization of TMC were done in a disc pelletizer of diameter 400 mm, collar height 100 mm Fig. 2 [7] , angle of inclination 60 °C, disc rotating speed 17 rpm and residence time 30 min. The TMC material was feed to the disc pelletizer then the predetermined moisture amount (10 % water) with different percentage of the charge molasses (1, 1.5, 2 and 2.5 %) was sprayed onto the rolling bed of material in the pelletizer. The green pellets in the size range 5-7 mm diameter were screened out to dry it for 72 hours in the air (in room temperature), to ensure the evaporation of all water used during the granulation process

Fig. 2. Disc pelletizer equipment

The green and dry pellets subjected to drop damage resistance and crushing strength tests. The crushing strength test used MEGA.KSC-10 hydraulic press) Fig.3 The drop damage resistance test indicates how often green and dry pellets can be dropped from a height 30 cm before they show perceptible cracks or crumble. Ten green and dry pellets are individually dropped on to a steel plate. The number of drops is determined for each pellets . The arithmetical average values of the crumbing behavior of the ten pellets yield the drop number[8-14] .The average compressive strength tests of at least 10 pellets; between parallel steel plates of MEGA.KSC up their breaking. The mean value of the tested pellets gives their compressive strength. [8-14]

Fig. 3. MEGA.KSC-10 hydraulic press

2.3. Reduction Procedures

The reduction of the produced pellets was performed in thermo gravimetric apparatus. This scheme is similar to that present elsewhere [6.15-20] (Figure 4). *It* consisted of a vertical furnace, electronic balance for monitoring the weight change of reacting sample and temperature controller. The sample was placed in a nickel chrome crucible which was suspended under the electronic balance by Ni-Cr wire. The furnace temperature was raised to the required temperature (600°C - 950°C) and maintained constant to ±5°C. Then samples were placed in hot zone. The nitrogen flow rate was 0.5 l/min pass through furnace in the beginning of the experimental to remove of the air from the furnace and then pass hydrogen with nitrogen one min then nitrogen stopped The weight of the sample was continuously recorded , at the end of the run; the samples were withdrawn from the furnace and put in the desiccators.
The percentage of reduction was calculated according to the following equations:
Percent of reduction = [(Wo –Wt) x100 / Oxygen mass]
Where:
Wo: the initial mass of the sample
Wt: mass of sample after each time, t.
Oxygen mass: indicates the total mass of oxygen percent in the sample in form FeO, Fe_2O_3 and manganese oxide.

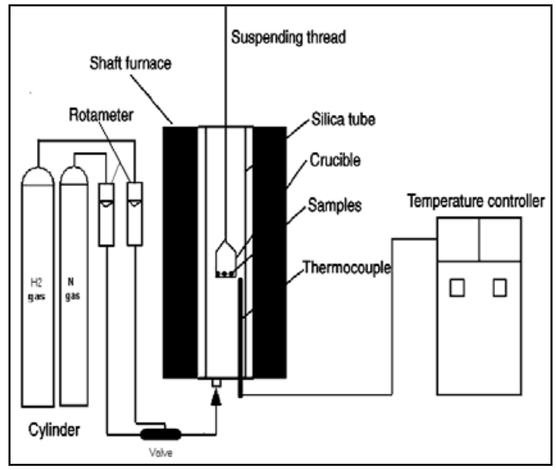

Fig. 4. Schematic diagram of the reduction apparatus

3. RESULTS AND DISCUSSION

3.1. Effect of The Different Amount of Molasses added to the material on The Quality of The Produced Pellets

In this experiment the 200 g TMC were pelletized in disc pelletizer with different amount of molasses where inclination of disc pelletizer = 55^{o}C and the produced pellets remained in the disc pelletizer for 30 minute. Figures (5) and (6) show the effect of amount of molasses added to TMC on the drop number and strength of the produced green pellets. From these figures it is clear that both drop number and crushing strength of the produced green pellets increased as molasses increased. Figures (7) and (8) show the effect of molasses added to TMC on the drop number and strength of the produced dried pellets for 3 days . From these figures it is clear that the drop number and the crushing strength of the produced dried pellets increased as the amount of molasses increased.

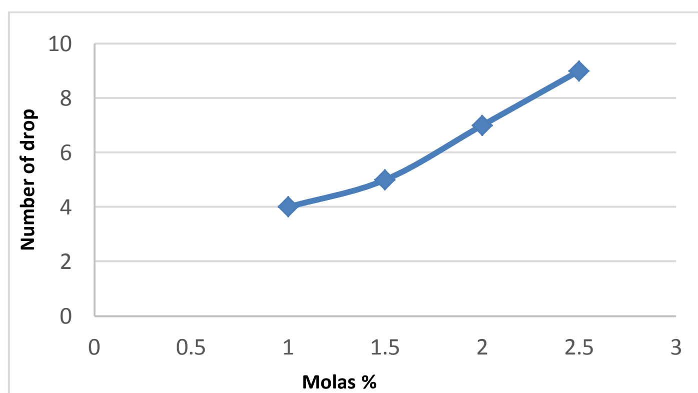

Fig. 5. Relationship between amounts of molasses added to TMC and drop number of the produce green pellets.

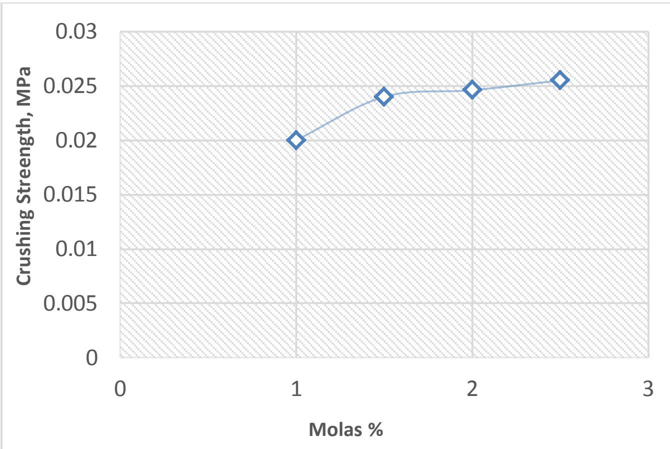

Fig. 6. Relationship between amounts of molasses added to TMC and strength of the produced green pellets.

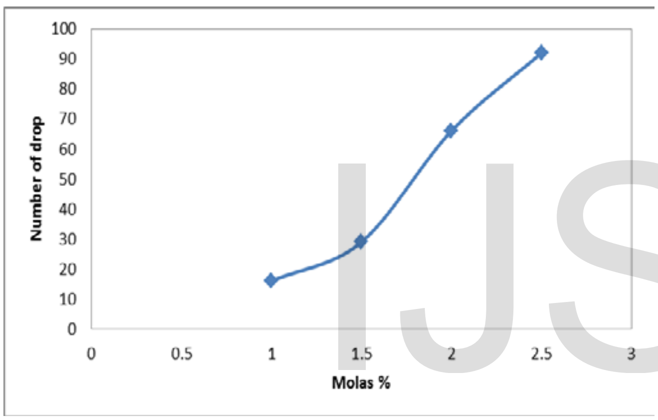

Fig. 7. Relationship between amounts of molasses added to TMC and drop number of the dried pellets.

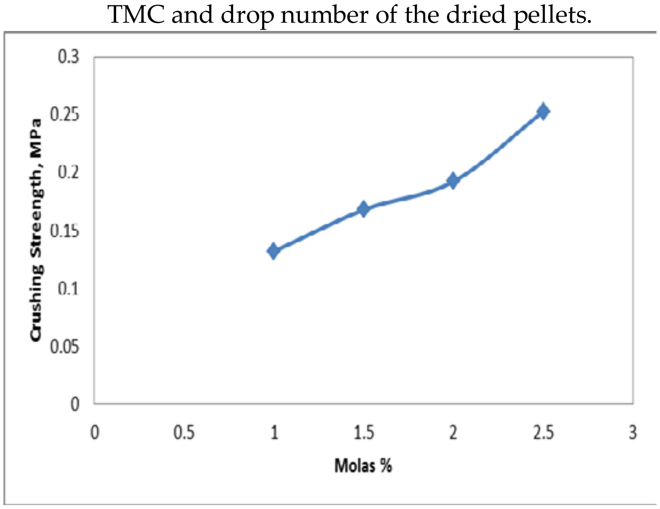

Fig. 8. Relationship between amounts of molasses added to TMC and drop number of the dried pellets.

3.2. Effect of Hydrogen Flow Rate on The Reducibility of Iron Oxides Content of Titanomagnetite Concentrate Pellets

In this part the dried pellets which of size 10 mm were reduced by hydrogen where the flow rate of the hydrogen was changed from (0.5 L to 2 L/ min.) while the reduction temperature was kept constant 900˚C. The results of these experiments were illustrated in Figure (9). From this figure it is clear that as the flow rate of hydrogen increased the reduction percentage increased This is probably due to the fact that increase of flow rate leads to increasing the 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 (21) or the increase of flow rate of hydrogen the gas diffusion across the boundary layer increased subsequently the reduction increased (22) . Also the higher flow rate prevailing in the reaction zone may enhances the rate of hydrogen absorption and subsequently the rate of chemical reaction steps increased(23)

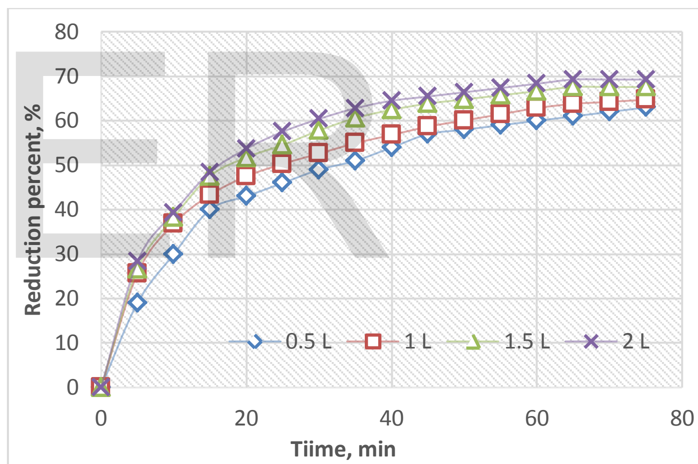

Fig. 9. Effect of reduction time on the percent of reduction by hydrogen of pellets (titanomagnetite concentrate + 2% molasses) at different hydrogen flow rates and 900˚C.

3.3. Effect of Reduction Temperatures on The Reducibility of Iron Oxides Content of Titanomagnetite Pellets

In this part the pellets of size 10 mm were reduced by hydrogen where the flow rate of hydrogen were kept constant (2 L/ min.) while the reduction temperature changed from 600 ˚C to 950˚C. The results of the investigation are shown in Figure (10) , where it is clear that the increase of temperature favors the reduction rate The analyze of the curves relating the reduction percentage and time of reduction show that each curve can be split into 3 different regions indicating 3 different values of reduction rates. The first value is high,

ISSN 2229-5518

while the second is somewhat slower and the third is the slowest one. The increase of reduction percentage with temperature is naturally due to an increase the number of reacting moles having excess energy which leads to the increase of adsorption rate (24 , 25*).* Also increasing temperature leads to increase the rate of mass transfer of the diffusion and rate of chemical reaction (22,23,26,27*).*

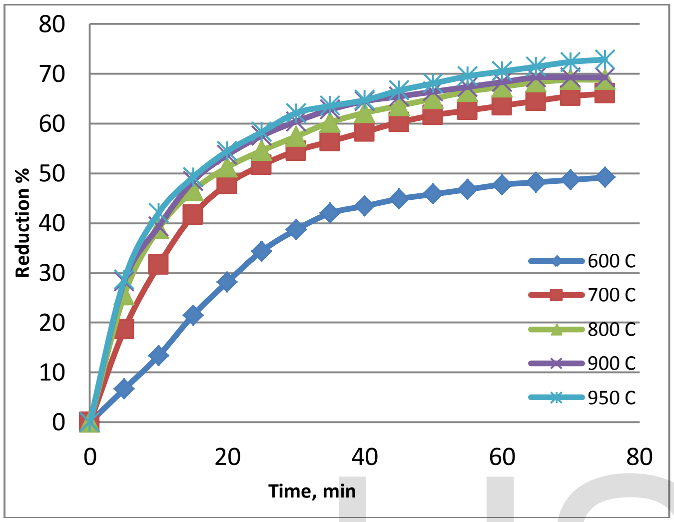

Fig. 10. Relationship between time of reduction and the percentage of reduction of TMG pellets at 2 l/min hydrogen flow rate and at different reduction temperature

3.4. The Kinetic Reduction of The TMC Pellets by Hydrogen

Kinetic studies for estimation of apparent activation energies were carried out for titanomagnetite concentrate produced from Rosetta illmenite ore pellets at five different temperatures of 600˚C, 700˚C, 800˚C, 900˚C and 950˚C for different time intervals in the range of 0 - 60 minutes.

1)By using (jander equation)

$$(1-(1-f)^{1/3})^2 = kt \qquad (1)$$

where f is fractional reduction, t is time of reduction, k is the rate constant.

Figure (11) illustrates the relation between $[(1-(1-f)^{1/3}]^2$ against time of reduction for different reduction temperature. From which it is clear that the relationship is represented by straight line.

2) When using diffusion process controls Equation (28)

$$1-{}^{2}/_{3}f-(1-f)^{\frac{2}{3}} = kt \qquad (2)$$

Figure (12) illustrates the relation between $[1-2/3f-(1-f)^{2/3}]$ against time of reduction for different reduction temperature. From which it is clear that the relationship is represented by straight line.

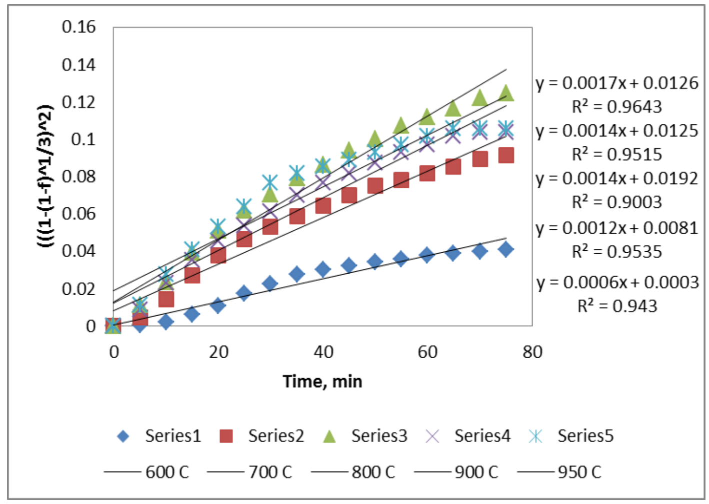

Fig. 11. Relation between [1-(1-f)1/3]2 (jander equation) and time of TMC reduction by hydrogen

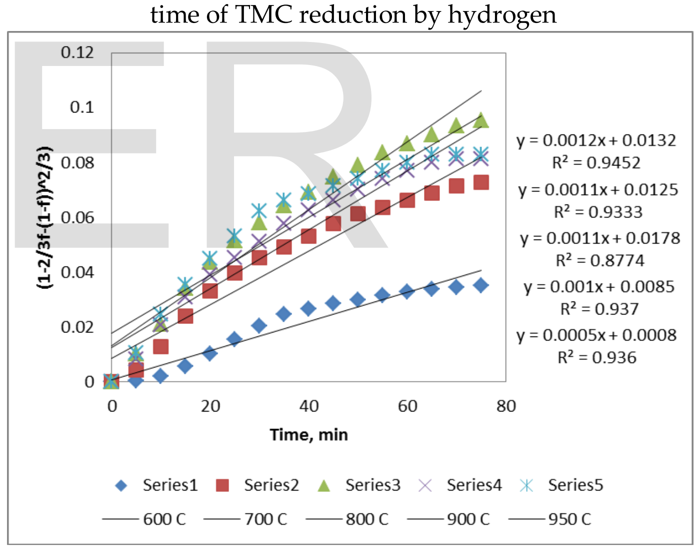

Fig. 12. Relation between $1-2/3f-(1-f)^{(2/3)}$ Diffusion controlled and time of TMC pellets reduction by hydrogen

The relationships between the natural logarithm of reduction rate constant and the reciprocal of absolute temperature for titanomagnetite concentrate pellets produced from Rosetta illmenite ore are shown in the following Figures 13-14 , from which it is clear that the activation energy = 31 kJ/mole for model $(1-(1-f)^{1/3})^2 = kt$ and the activation energy for model $1-{}^{2}/_{3}f-(1-f)^{\frac{2}{3}} = kt$= 22.77 kJ/mole respectively.

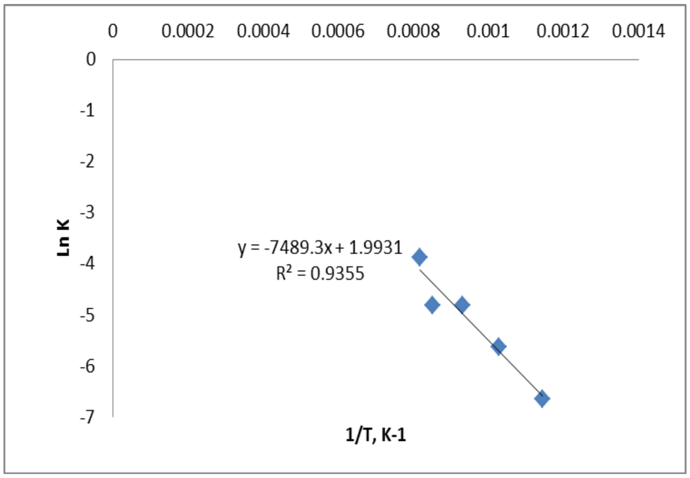

Fig. 13. Relation between ln k and 1/T for the models Diffusion through thin ash layer [1-(1-f)1/3]2 (jander equation)

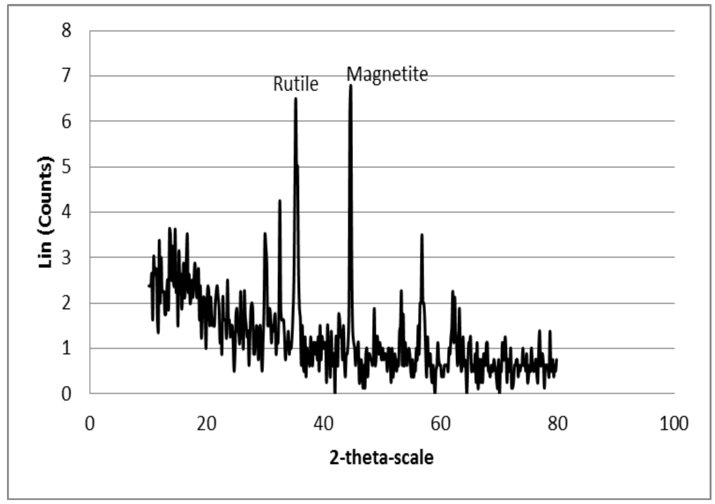

Fig. 15. XRD of TMC pellets reduced by hydrogen at 600 °C

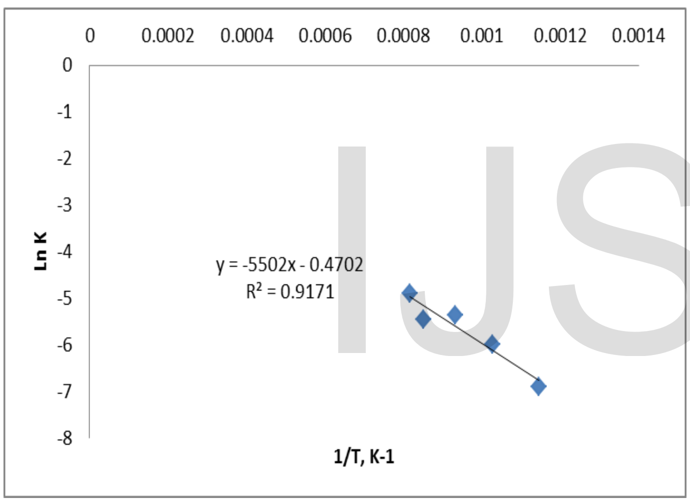

Fig. 14. Relation between ln k and 1/T for the models of Diffusion controlled

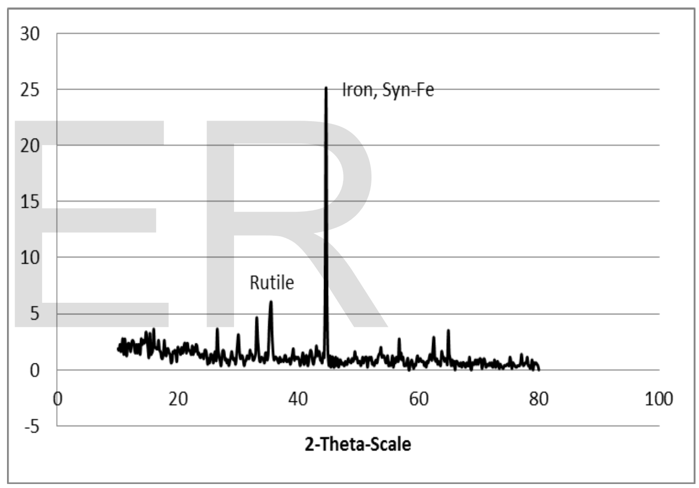

Fig. 16. XRD of TMC pellets reduced by hydrogen at 950°C

3.5. X-Ray Analysis of The Reduced Pellets by Hydrogen

Figures (15 and 16) illustrates x-ray analyses of reduced TMC pellets at temperature (600 ° C) and (950˚C) in hydrogen atmosphere. From these figures it is clear that the reduction at 600 ° C have low amount of iron and more magnetite present in the structure while at 950 °C more amount of metallic iron is produced in the sample with some rutile .

4. CONCLUSIONS

1- The higher mechanical properties of dried titanomagnetite concentrate pellets occurs by using 2.5% molasses with 8.5 % water as moisture content .

2- The reduction rates of TMC increased with increasing temperature of the reduction from 600 up to 950°C.

3- The reduction rate increased with increased of hydrogen flow rate at constant reduction temperature.

4- The reduced pellets at 600 ° C have low amount of iron and more magnetite and rutile present in the structure while which reduced at 950 °C have more amount of metallic iron is produced in the sample with some rutile .

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