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Onuralp Yucel*, Fahri Demirci, Ahmet Turan and Murat Alkan

Determination of Direct Reduction Conditions of Mill Scale

Abstract: In this study, experiments were conducted to understand the optimum direct reduction conditions of mill scale which is formed on the surface of the materials produced by continuous casting and which contains iron (II) and iron (III) oxides. Experiments were performed in a rotary kiln and anthracite and metallurgical coke were used as carbon source. The eligible parameters like process temperature, process duration, reductant type and quantity were tried to determine. Obtained reduced iron pellets were characterized by using EPMA, XRD and chemical analysis techniques. The highest metallization degrees were observed as 97.4% for the stoichiometrically 200% anthracite added experiments and as 95.5% for the stoichiometrically 200% metallurgical coke added experiments at 1423 K.

Keywords: mill scale, direct reduction, sponge iron

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***Corresponding author: Onuralp Yucel:** Metallurgical and Materials Engineering Department, Faculty of Chemical and Metallurgical Engineering, Istanbul Technical University, 34469, Maslak, Istanbul, Turkey. E-mail: yucel@itu.edu.tr
Fahri Demirci, Murat Alkan: Metallurgical and Materials Engineering Department, Faculty of Chemical and Metallurgical Engineering, Istanbul Technical University, 34469, Maslak, Istanbul, Turkey
Ahmet Turan: Metallurgical and Materials Engineering Department, Faculty of Chemical and Metallurgical Engineering, Istanbul Technical University, 34469, Maslak, Istanbul, Turkey; Yalova Community College, Yalova University, 77100, Yalova, Turkey

1 Introduction

Mill scale is an iron oxide layer which forms on the surface of steel continuous casting products during the process. This layer contains a mixture of iron (II) and iron (III) oxides with high iron content.

Direct reduction process (DR) is a relatively new process which is employed to produce iron from ferrous raw materials by gaseous or solid reductants below the melting point of the feed. The product of the process is called ‘Direct reduced iron’ (DRI). DRI has a low level of the gangue compounds, so it is eligible to use in electric arc furnace (EAF) and blast furnace (BF) as a feed. World DRI production is reported as 70.4 Mt in 2010 with a growth of 60% during the last decade [1, 2 and 3].

The subject of the process is the reduction of iron oxide to metallic iron in solid state at relatively low temperatures about 1273 K. Use of raw materials in the form of ore lumps, fine ores and pellets is available. Gaseous and solid carbon sources can be employed as a reductant. The type of reductant is the main parameter which determines the route of process such as MIDREX and HYL III processes using gaseous reductant. Metallization degrees were reported around 85–95% according to process conditions [1, 2].

Kopfle et al. were reported the main advantages of DR process as lower investment costs and use of lump iron ore, fine ore and coal without any prior preparation and treatment. Recent studies show that the impurities like oil in the mill scale and volatile materials in the solid carbon sources have a positive contribution on the increase of metallization degrees during the DR process [4, 5 and 6].

In this study, optimum conditions to produce highly metalized DRI from the mill scale formed on a continuous casting facility were investigated. The use of mill scale as a ferrous material source is a new study field in DR technology which is going to contribute for the recycling of sources and waste management. The reduction process was carried out in a rotary kiln. The experiments were designed to determine the process parameters regarding to temperature, duration, reductant type and the amount of the reductant.

2 Theoretical background

DR is a well studied process in terms of reactions, thermodynamics and kinetics. Zervas et al. classified the dominant reactions which occur during the process. The dominant reactions below about 1273 K are given below [7]:

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O \quad (1)$$

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \quad (2)$$

$$Fe_3O_4 + H_2 \rightarrow 3FeO + H_2O \quad (3)$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \quad (4)$$

$$FeO + H_2 \rightarrow Fe + H_2O \quad (5)$$

$$FeO + CO \rightarrow Fe + CO_2 \quad (6)$$

Additional reactions are [7]:

$$3Fe + CO + H_2 \rightarrow Fe_3C + H_2O \quad (7)$$

$$3Fe + 2CO \rightarrow Fe_3C + CO_2 \quad (8)$$

At temperatures above about 1273 K following reactions begin to occur and the reaction which is according to Eq. (11) has a very considerable role which causes to produce DRI through the solid carbon without any gaseous reductant [7]:

$$CO_2 + C \rightarrow 2CO \text{ (Boudouard reaction)} \quad (9)$$

$$H_2O + C \rightarrow CO + H_2 \quad (10)$$

$$FeO + C \rightarrow Fe + CO \quad (11)$$

From 1473 K, the reaction which is according to Eq. (12) begins and this is the theoretical upper temperature limit for the DR process due to the melting of the charge [7]:

$$3Fe + C \rightarrow Fe_3C \quad (12)$$

A Bauer-Glaessner diagram, which contains the reactions classified above as Eqs. (2), (4), (6), (8) and (9), was drawn by using the conversion of Gibbs free energy values, taken from FactSage 5.4, to CO partial pressure for each reaction and temperature. The diagram is given in Figure 1.

An equilibrium state diagram which is for Fe-C-O system at 1173 K, 1273 K and 1373 K was plotted by the authors using FactSage 5.4 and it is given in Figure 2. As shown in the diagram, FeO and Fe stability zones expand with the increase at the temperature. Reaction products change from Fe_3O_4 zone to FeO and Fe zones respectively with the increase in CO partial pressure for 1 atm (101.325 kPa) constant pressure. Fe_3C phase which is very stable against oxidation just occurs under very high CO partial pressure and very low CO_2 partial pressure for high atmosphere pressures. Increase in the temperature has a negative effect on the phase stability of Fe_3C.

Liu et al. determined the reduction temperatures of Fe_2O_3 to Fe_3O_4, Fe_3O_4 to FeO and FeO to metallic Fe as 773–943 K, 1013–1143 K and 1143–1473 K respectively for DR process by using CO and H_2 as products of coal devolatilization and char gasification [8].

Geçim et al. were calculated activation energies for a DR process which was designed to reduce pelletized iron ore by using lignite coal reductants as 103.41 kJ/mol for 100% stoichiometry and 86.67 kJ/mol for 133% stoichiometry [9].

3 Experimental

The mill scale which was used for the experiments comprises very high amount of iron (II) and iron (III) oxides. XRD pattern (PANalytical PW3040/60) of the mill scale is

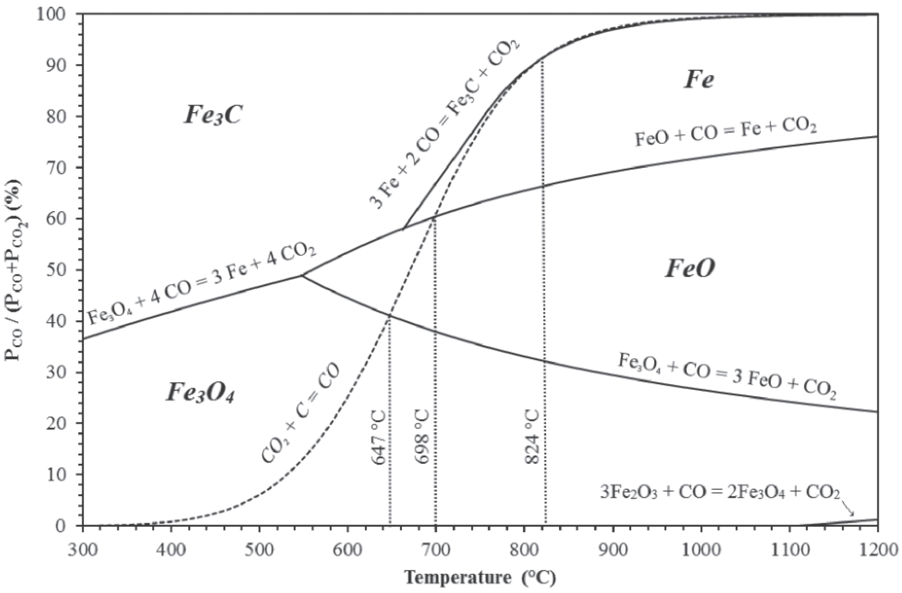

Fig. 1: A Bauer-Glaessner diagram simulated by using FactSage 5.4 data

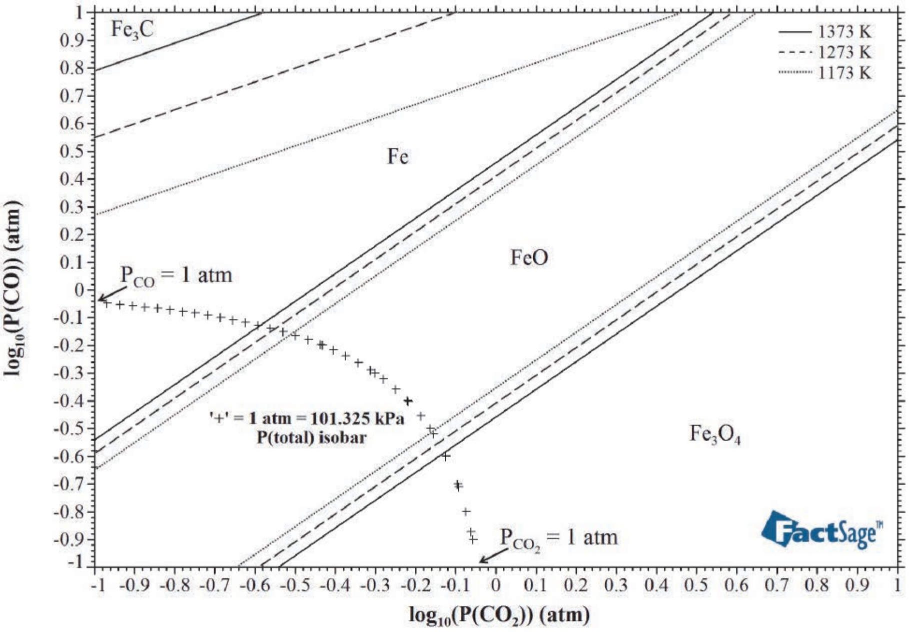

Fig. 2: Equilibrium states of Fe-C-O system at 1173 K, 1273 K and 1373 K plotted by using FactSage 5.4

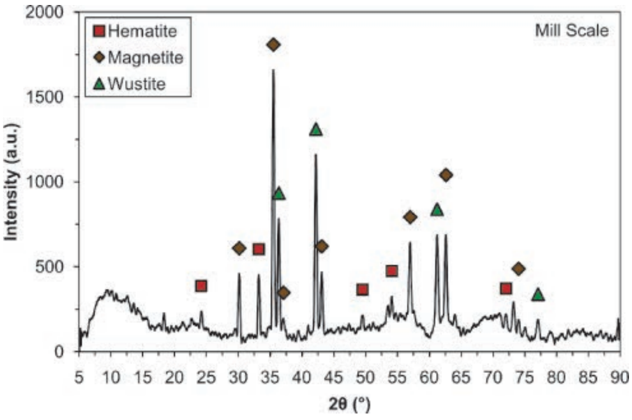

Fig. 3: XRD pattern of the Mill Scale

Table 1: Chemical composition of the Mill Scale

Component	Weight (%)
Total Fe	70.95
Fe^{2+}	24.59
Fe^{3+}	42.80
Fe^{0}	3.56
Cu	0.14
Mn	0.75
Si	0.19

Table 2: Chemical compositions of the reductants

Reductant type	Fixed carbon (%)	Volatile matter (%)	Ash (%)	Sulfur (%)
Anthracite	86.87	3.97	8.75	0.41
Metallurgical coke	89.18	3.07	6.78	0.96

shown in Figure 3 and the chemical composition is given in Table 1. Anthracite and metallurgical coke are the reductants which were employed as a carbon source; Table 2 gives their chemical compositions. Raw materials were ground until the size range of 45–90 μm to homogenize before the experiments.

Pelletizing process was applied to ground mill scale which was mixed with 5% by wt. molasses as a binder. Molasses was employed to enhance the strength of the pellets in the furnace; it is also substantially inactive on the reduction of pellets and the formation of slag. Pelletizing process was performed using a lab-scale pellet disc. Obtained pellets were dried at 378 K for 5 hours.

Reductants were mixed with the pellets as respectively 150% and 200% of the stoichiometrically required amount for each reductant type. The amount of used reductants were calculated from the amounts of fixed carbon which is seen in Table 2 according to the stoichiometrical reactions of iron (II) and iron (III) oxides (given in Table 1) with CO.

Direct reduction experiments were conducted in a semi-pilot scale rotary kiln (RUHSTRAT, SiC resistance) in a steel retort. Further information about the used rotary kiln system can be found elsewhere [10, 11]. The quantities of charged materials are shown in Table 3. Maximum experiment duration was designed as 120 minutes and

Table 3: Quantities of used charge materials

Stoichio. (%)	Anthracite (g)	Metallurgical coke (g)	Mill Scale pellets (g)
150	329	320	1000
200	438	426	1000

samples were taken at the 5th, 10th, 15th, 30th, 45th, 60th, 90th and 120th minutes to investigate the relationship between the metallization degree and the reaction duration. 1323 K, 1373 K and 1423 K were chosen reaction temperatures to conduct the experiments. Characterization of reduced samples was performed by using EPMA (Electron Probe Micro Analyzer), XRD and the chemical analysis methods. As a result of analyses, metallization degrees for each sample were determined according to the equation which is given in Eq. (13) where Fe_{Me} is the mass of metallic iron in the pellet and Fe_{Total} is the mass of the total iron of mill scale in the charge.

$$\text{Metallization } \% = (Fe_{Me} / Fe_{Total}) \times 100 \qquad (13)$$

4 Results and discussion

According to the results, metallization degrees increase with the increase in reaction time. Increasing process temperature has an effect causing the increase in metallization degrees as well. The highest metallization degrees were determined at 120th minute for each experimental set and grouped results can be seen in Table 4.

Figure 4 and Figure 5 indicate the change on the metallization degrees with increasing process time and temperature (1323 K, 1373 K and 1423 K) for the anthracite

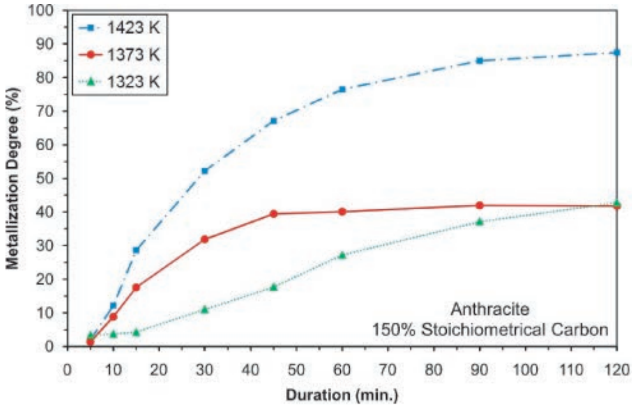

Fig. 4: Metallization degrees of the samples with the increase of reaction time and anthracite added as 150% of the stoichiometrically required amount at temperatures of 1323 K, 1373 K and 1423 K

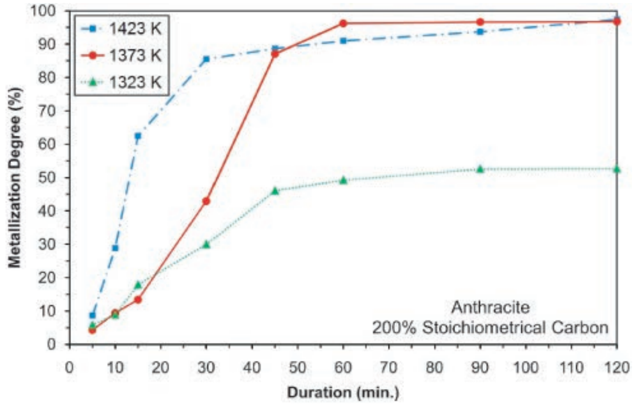

Fig. 5: Metallization degrees of the samples with the increase of reaction time and anthracite added as 200% of the stoichiometrically required amount at temperatures of 1323 K, 1373 K and 1423 K

Table 4: Metallic iron and total iron contents and metallization degrees of the final samples at 120th minute

Temp. (K)	Reductant type	C Stoichio. (%)	Metallic Fe (%)	Total Fe (%)	Metallization (%)
1323	Anthracite	150	34.5	80.7	42.7
1373	Anthracite	150	35.3	84.3	41.8
1423	Anthracite	150	80.9	92.6	87.4
1323	Anthracite	200	43.8	83.2	52.6
1373	Anthracite	200	88.8	91.8	96.8
1423	Anthracite	200	89.0	91.4	97.4
1323	Met. coke	150	58.0	87.4	66.4
1373	Met. coke	150	80.0	90.6	88.3
1423	Met. coke	150	83.5	88.0	94.9
1323	Met. coke	200	71.8	83.6	85.5
1373	Met. coke	200	81.5	91.7	89.0
1423	Met. coke	200	92.0	96.4	95.5

added samples as 150% and 200% of the stoichiometrically required amount respectively. Metallization degrees were determined in the samples as 87.4% on 150% anthracite added run and 97.4% on 200% anthracite added run which both taken at 120th min. and 1423 K. Increase in metallization degrees with the increase in temperature are the results of acceleration in chemical reactions and diffusion at higher temperatures. The change of reductant to gaseous state has also a significant effect on the rapid increase in metallization degree initially. The reason on the constant metallization degrees after a rapid increase can be explained as the decrease in CO partial pressure in the furnace atmosphere and the preventing of the gas diffusion into the center of the pellets due to nonporous reduction products. For the anthracite used experiment sets, it is very clear to see that increase in the reductant amount critically increase the metallization degrees.

Maximum metallization degrees were observed as 94.9% and 95.5% for the metallurgical coke employed samples as 150% and 200% of the stoichiometrically required amount respectively at 120th min. and 1423 K. Similar to anthractite added experimental sets, metallization degrees increase with the increase in process temperature and reaction time. Results are given in Figure 6 and Figure 7 as graphs.

R values were calculated using chemical analysis results of the samples which were taken with increasing reaction time for the kinetic investigation of the experiments. Graphics were drawn between the term $[1-(1-R)^{1/3}]$ and reaction time for anthracite and metallurgical coke added samples with 150% and 200% stoichiometric ratios. Process time was limited to the duration lower than 60 minutes when most of the reduction occurs. Moreover, the kinetic investigation results which lower than 10th minute were not given with the calculations due to the unstable area at the temperatures in question. The graphics of stoichiometrically 200% reductant added experiments can be seen in Figure 8 and Figure 9. The linearity in the graphics indicates kinetic results are in accordance with the Eq. (14) and reactions are chemically controlled. Reaction constants were calculated from the Figure 8 and Figure 9 and adapted to the graphics which were given in Figure 10 and Figure 11. Activation energies, for the experiments anthracite and metallurgical coke added as 150% and 200% of the stoichiometrically required amount at temperatures of 1323 K, 1373 K and 1423 K, were calculated using Arrhenius Equation (Eqs. (15) and (16)). Activation energy values of all experimental sets are shown in Table 5.

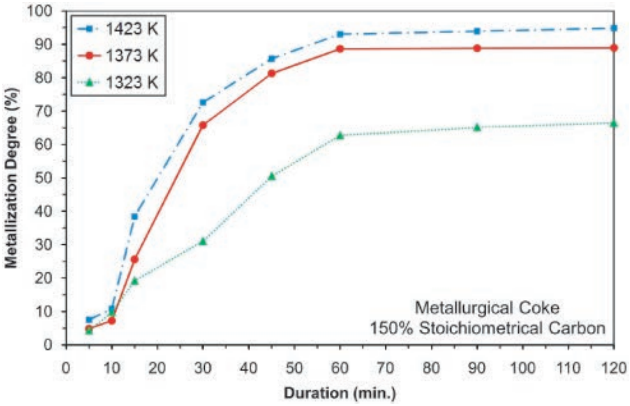

Fig. 6: Metallization degrees of the samples with the increase of reaction time and metallurgical coke added as 150% of the stoichiometrically required amount at temperatures of 1323 K, 1373 K and 1423 K

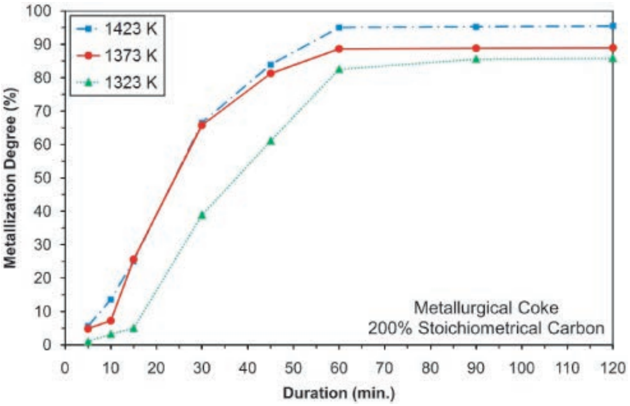

Fig. 7: Metallization degrees of the samples with the increase of reaction time and metallurgical coke added as 200% of the stoichiometrically required amount at temperatures of 1323 K, 1373 K and 1423 K

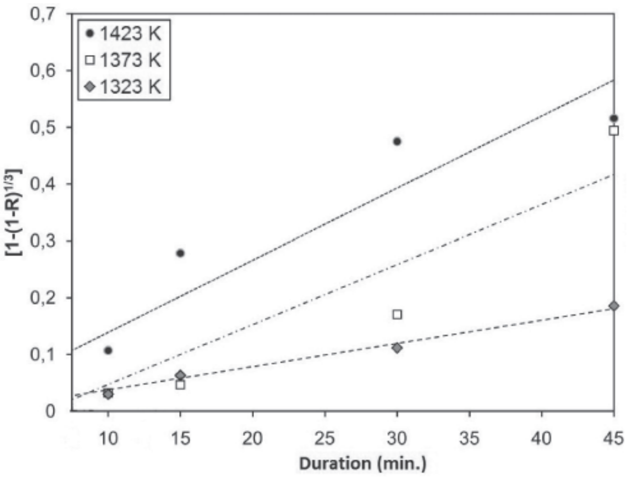

Fig. 8: Change of the term $[1-(1-R)^{1/3}]$ with reaction time for anthracite added experiments as 200% of the stoichiometrically required amount at temperatures of 1323 K, 1373 K and 1423 K

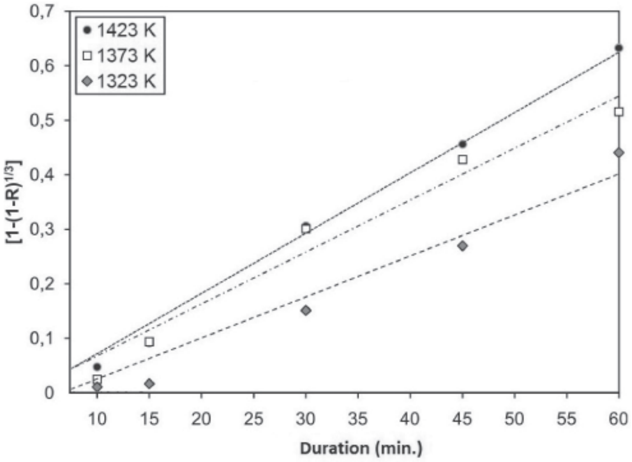

Fig. 9: Change of the term $[1-(1-R)^{1/3}]$ with reaction time for metallurgical coke added experiments as 200% of the stoichiometrically required amount at temperatures of 1323 K, 1373 K and 1423 K

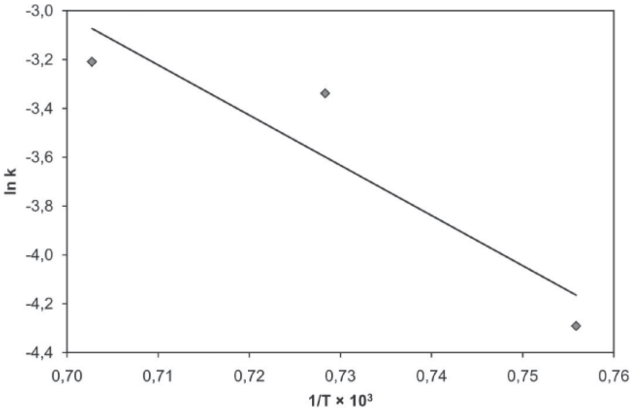

Fig. 10: Change of the reaction constants with reaction time for anthracite added experiments as 200% of the stoichiometrically required amount at temperatures of 1323 K, 1373 K and 1423 K

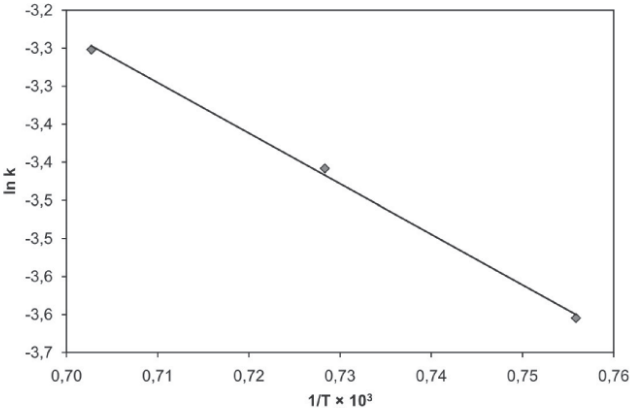

Fig. 11: Change of the reaction constants with reaction time for metallurgical coke added experiments as 200% of the stoichiometrically required amount at temperatures of 1323 K, 1373 K and 1423 K

Table 5: Calculated activation energies of conducted experiments

Stoichio. (%)	Reductant (g)	Activation energy (kJ/mol)
150	Anthracite	316.06
200	Anthracite	170.78
150	Met. Coke	127.03
200	Met. Coke	55.22

$$[1-(1-R)^{1/3}] = kt \tag{14}$$

$$k = A.e^{-E/RT} \tag{15}$$

$$k = \ln A - (E/RT) \tag{16}$$

The comparison between the anthracite and metallurgical coke added experiments indicate that there is higher metallization rate for the anthracite added samples on stoichiometrically 200% reductant added samples at 1423 K. This is the reason of the rapid change of metallurgical coke to the gaseous state and the higher reduction capability of the anthracite at high temperatures. Reduction of anthracite and metallurgical coke utilized pellets to the metallic state can be seen in Figure 12 for 200% reduc-

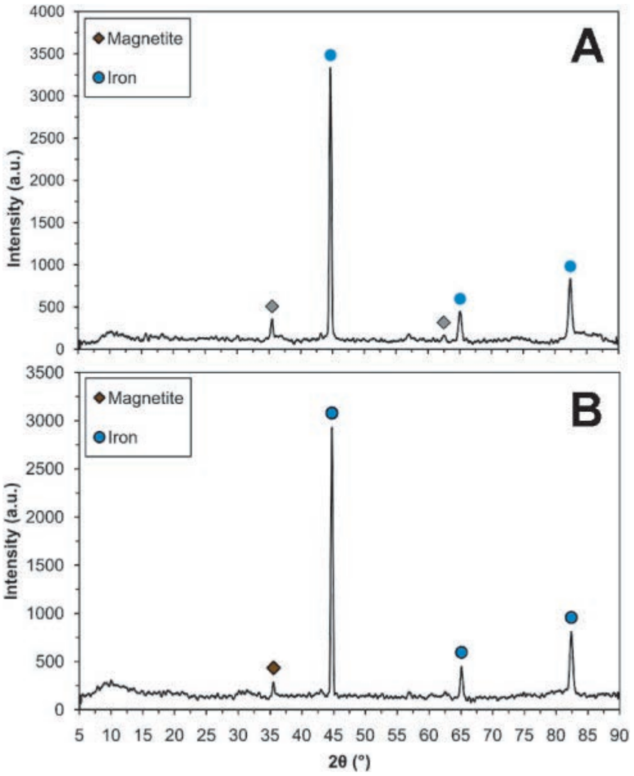

Fig. 12: XRD patterns of direct reduced Mill Scale pellets which were processed at 1423 k and 120th min.; (a) anthracite added as 200% of the stoichiometry, (b) metallurgical coke added as 200% of the stoichiometry

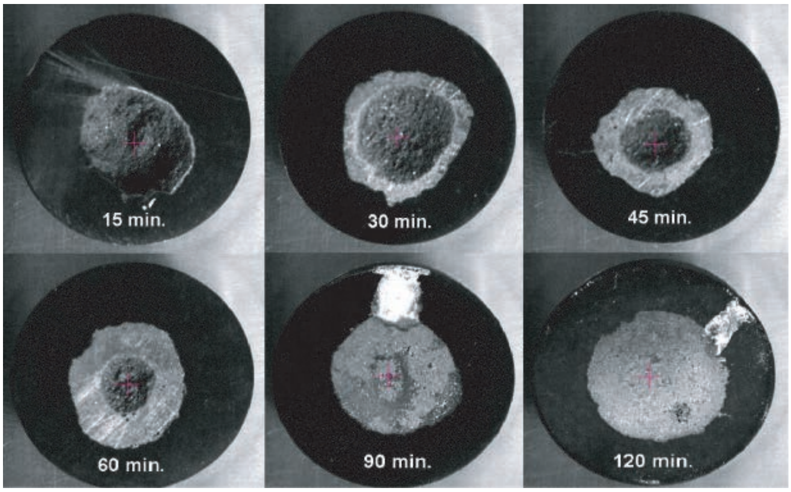

Fig. 13: Reduction of Mill Scale pellets with the increase in reaction time; reduction occurs from the surface to the center of the pellets (samples are metallurgical coke added as 200% of the stoichiometry at 1423 K)

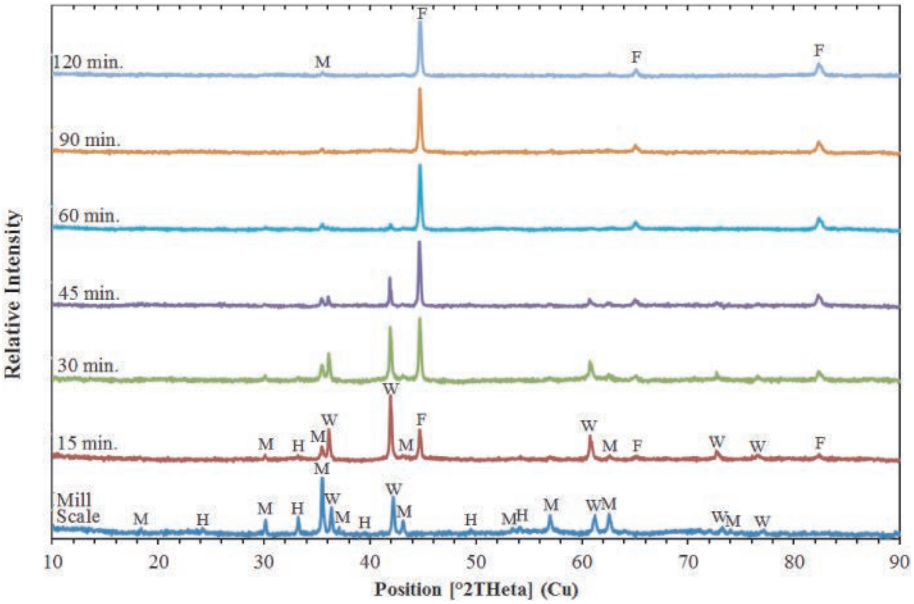

Fig. 14: XRD patterns of direct reduced Mill Scale pellets which indicate increase in metallization degrees with the increase in reaction time (letters refer to different phases; M for Magnetite, H for Hematite, W for Wustite and F for Metallic Iron. Samples are metallurgical coke added as 200% of the stoichiometry at 1423 K).

tant added samples at 1423 K and 120th minute. The effect of process time on reduction is given in Figure 13 and Figure 14.

5 Conclusion

- Iron oxide in the mill scale was reduced using direct reduction process in a rotary kiln. The investigated parameters were process temperature (1323 K, 1373 K and 1423 K), process time (from 0 to 120 min.), reductant type (anthracite, metallurgical coke) and reductant stoichiometry (150% and 200%).
- The metallization degrees of the samples obtained during experiments were observed to increase consistently with increased reduction duration and higher process temperature.
- An increase in metallization degrees was observed with the increase in stoichiometrically used amount of the reductants; it was very significant for the anthracite used experiments and slightly for the metallurgical coke used experiments.

- The highest metallization degrees were observed as 97.4% for the stoichiometrically 200% anthracite added experiments and as 95.5% for the stoichiometrically 200% metallurgical coke added experiments at 1423 K, although metallurgical coke is more efficient in terms of the reduction until the high temperatures in question. It is thought that metallurgical coke has high tendency to change into the gaseous state, however anthracite has higher reduction capability at high temperatures.
- Activation energies were calculated for the experiments stoichiometrically 200% anthracite added as 170.78 kJ/mol, 150% anthracite added as 316.06 kJ/mol, 200% metallurgical coke added as 55.22 kJ/mol and 150% metallurgical coke added as 127.03 kJ/mol at 1323 K, 1373 K and 1423 K.

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