CHAPTER IV

PROCESSING OF IRON NUGGET FROM LOW GRADE IRON ORE

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Abstract

Nowadays, the sources of high grade iron ore are quite rare and limited. A new technology which can produce iron nuggets is known as "Iron making Technology Mark Three" (ITmk3). Our objective is to modify the ITmk3 process to produce iron nuggets from a low grade iron ore and to determine the suitable parameters which control the quality of the iron nuggets: the weight ratios of feeds, the reduction time, and the reduction temperature. The ultimate goal of this work is to determine the most suitable conditions to produce iron nuggets from low grade iron ore which has 50–60% iron content and a low grade coal as the raw materials. The most suitable conditions for making Iron nugget (over 94 % Fe and % yield more than 94 %), from a pellet which has a diameter of 2.5 cm and 4 cm high, are by using the mol ratios of the mixture of C/Fe = 1.53, Limestone/Al2O3+SiO2 = 0.75, and Bentonite/Fe = 0.02/1 with the reduction temperature of 1425°C and at the reduction time of 20 min.

Keywords: Iron Nugget, Iron making Technology Mark Three, Direct reduction, Low grade Iron ore, Hematite

Introduction

World economic expansion has an effect on the steel demand; as a consequence, the global steel production has been growing yearly. The principal concern for iron suppliers today is the issue of the tight raw material supply. Kobe Steel and Midrex have arrived at a viable solution for this concern through a new technology known as IT Mark Three (ITmk3), based on their coal-based direct reduction technologies that have been in development over the past decade. ITmk3 is a unique process that, in a rotary hearth furnace, turns iron ore fines and a pulverized coal into iron nuggets of the same quality as the blast furnace pig iron (Tanaka, 2008 and Midrex Technologies, 2009).

The ITmk3 Process has many advantages, and is very flexible regarding carbon sources. The process can use coal, petroleum coke, or blast furnace dust, and other forms of solid, liquid and gaseous reductants. It is, environmentally friendly technology for producing a high quality iron product, of low capital investment, and highly suitable for developing countries that are growing in their steel industries. In addition, the ITmk3 Process can use relatively low-grade iron ore and coal, which are difficult to use in the blast furnace iron making, to keep raw material costs down where mining companies traditionally supply raw but expensive materials to integrated blast-furnace steelmakers (Negami, 2001).

The ITmk3 process has reactions taking place inside the pellet:

$$3Fe_2O_3 + CO \leftrightarrow 2Fe_3O_4 + CO_2 \quad (1)$$

$$Fe_3O_4 + CO \leftrightarrow 3FeO + CO_2 \quad (2)$$

$$FeO + CO \leftrightarrow Fe + CO_2 \quad (3)$$

$$Fe_2O_3 + 3CO \leftrightarrow 2Fe + 3CO_2 \quad (4)$$

$$C + O_2 \leftrightarrow CO_2 + \text{Heat} \quad (5)$$

$$C + \frac{1}{2}O_2 \leftrightarrow CO + \text{Heat} \quad (6)$$

$$C + CO_2 \leftrightarrow 2CO \quad (7)$$

$$CaCO_3 \leftrightarrow CaO + CO_2 \quad (8)$$

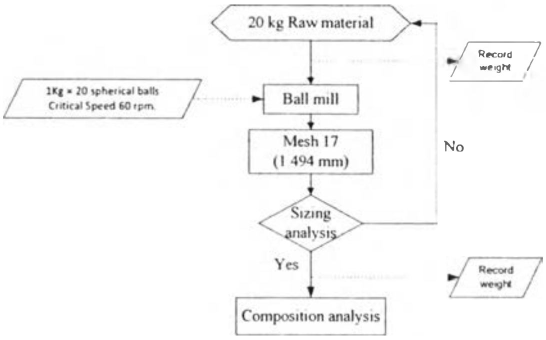
The reducing gas forming reactions, carbon monoxide, are shown in the reactions 5–7 with the solid Hematite, (Fe_2O_3) is represented by reactions 1–3. The steps of reducing Hematite to iron can be combined into the reaction (4).The endothermic; reaction 7 is activated at very high temperatures. The flux forming (CaO) is shown in the reaction 8. (Binayak et al., 2009 and Anameric et al., 2005)

The purpose of this work is to study the ITmk3 process and to determine the parameters which control the quality and quantity of iron nuggets on a laboratory scale by using a low grade iron ore which has 50–60% iron content and a low grade coal which has 40 % fixed carbon as the raw materials. In this study, a bentonite was used as a binder. The parameters: the weight ratios of mixture, the reduction time and the reduction temperature were varied to determine the most suitable conditions.

Experimental

Raw Materials

Iron ore from Xieng Khouang Lao PDR was the source of the iron oxide for the iron production. In our case, the low grade Iron ore has % Fe 55.99 %, (XK-01). Reductant is a substance used to reduce oxygen in an iron ore. In our case, the Dai coal, obtained from Xieng Khouang Lao PDR has a fixed carbon content of 40 %. Limestone is a flux used to separate iron from slag or other components. Limestone from CP® (Thailand) (99.08 % wt $CaCO_3$) was used in our experiment. The sodium bentonite from Volclay Siam Ltd. was a binder used in our experiments.



Scheme 1 Grinding step.

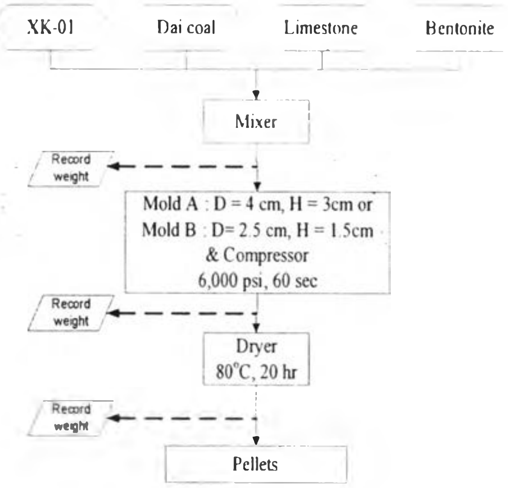
Sample Preparation

Grinding *of raw materials*

XK-01 iron ore and the Dai coal were grinded by a dry cylindrical ball mill in which the chamber has a diameter 70 cm and a length 100 cm. The step of grinding is shown in Scheme 1. The particle size after grinding was measured by SEM (Hitachi, model S-4800).

Mixing and the Pellet Preparation

XK-01, Dai coal, Limestone, Bentonite were mixed where amounts of the raw materials in the mixtures are shown in Table 7. Water of 10 % by weight of the mixture was added to the mixture of the raw materials. The mixture was well mixed until a homogenous mixture and the mixture was fed into a cylindrical mold which has a diameter of 4 cm and 7 cm high for making pellets. The steps of the pellet preparation are shown in Scheme 2.



Scheme 2 Step of pellet preparation.

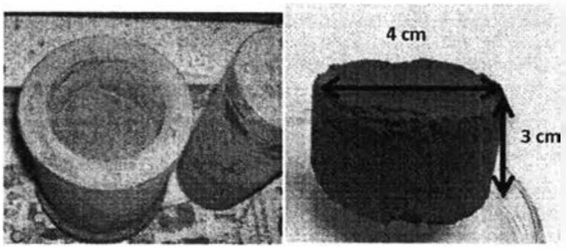


Figure 1 Mold and sizes of the pellets.

Table 1 The mol ratios and the weights of the raw materials in the mixtures.

Experiments	No.	Mol ratio				Weight (g)			
		Fe	C/Fe	Limestone /Al_2O_3+SiO_2	Bentonite /Fe	XK-01	Dai coal	Limestone	Bentonite
1.Effect of the reduction time and reduction temperature	1–19	1	1.72	0.89	0.02	300.05	155.53	29.79	4.20
2.Effect of mol ratio C/Fe	1	1	1.24	0.89	0.02	200.00	74.87	19.86	2.80
	2		1.34				80.63		
	3		1.44				86.39		
	4		1.53				92.15		
	5		1.63				97.91		
	6		1.72				103.67		
	7		1.82				109.43		
	8		1.91				115.19		
3.Effect of mol ratio Limestone/Al_2O_3+SiO_2	1		1.53	0.50			92.15	11.20	
	2			0.60				13.39	
	3			0.70				15.62	
	4			0.75				16.80	
	5			0.89				19.86	
	6			1.00				22.31	
	7			1.26				28.00	
	8			1.76				39.21	
	9			2.26				50.41	

Reduction

All of the pellets was reduced by a furnace (Nabertherm,HTCT 08/15) and fed at a reduction temperature which was held on during the reduction period. After the reduction period, the sample was taken out immediately. Experiment 1, the pellets were reduced at the reduction temperature in range of 1375–1500°C and the reduction time of 50 min to determine the suitable conditions. Experiment 3, (all pellets were reduced at the suitable reduction time and the reduction temperature from Experiment 1) the mol ratios C/Fe and Limestone/Al_2O_3 of the mixture were varied to minimize the raw materials usage as tabulated in Table 1.

Characterization

The XK-01 and the products were characterized for the wt % of elements by an Energy Dispersive X-Ray fluorescence spectrometer (Horiba, model 51-ADD0014), connected to a scanning electron microscope (Hitachi, model S-4800, 25

V, 20 mA). The structures of XK-01, the Dai coal, and the output product were characterized by an X-Ray diffraction spectrometer (Rigaku D/max; model 2000).The particle sizes after grinding were measured by a scanning electron microscope (Hitachi, model S-4800). The XK-01 iron ore was also analyzed for its compositions by the Wet Chemical Analysis at the Rock and Mineral Analysis Department of Mineral Resources, Ministry of Natural Resources and Environment Thailand and Dai coal was analyzed by the Proximate Analysis by the Electricity Generating Authority of Thailand. The product from the best condition was analyzed the microstructure by etching (2 % Nital, 3 sec) and a backscattered scanning electron microscope.

Results

Raw Material Characterization

The Characteristic of the raw materials are tabulated in Tables 2–7.

Table 2 Composition of the XK-01 iron ore by the Wet Chemical Analysis from the Rock and Mineral Analysis Department of Mineral Resources, Thailand.

Composition	% wt
Fe_2O_3	80.95
FeO	1.28
SiO_2	4.34
Al_2O_3	1.65
CaO	0.14
MgO	0.05
Na_2O	0.06
K_2O	0.16
H_2O	0.57
Others	10.8

Table 3 % Wt Element of XK-01 by Energy Dispersive X-Ray Fluorescence (Horiba, model 51-ADD0014). The accelerating voltage, current and magnification were 25 kV, 20 μA and 100X, respectively.

Elements	Average % wt	SD
C	5.95	4.52
O	32.70	0.98
Al	1.69	0.10
Si	2.28	0.26
K	0.26	0.06
Fe	55.99	5.60
Zr	0.87	0.05
Mn	0.00	0.00
Ca	0.00	0.00
Ti	0.03	0.03
Au	0.00	0.00
Cu	0.05	0.05
P	0.18	0.06
S	0.00	0.00
Mg	0.00	0.00
Na	0.00	0.00

Table 4 Proximate Analysis of the Dai coal.

	Parameter	Unit	Method	Result
As received basis	Moisture	% by weight	ASTM D3302-02a^{S1}	21.29
	Ash	% by weight	ASTM D5142-09	5.97
	Volatile matters	% by weight	ASTM D5142-09	35.47
	Fixed carbon	% by weight	ASTM D5142-09	37.26
	Sulphur	% by weight	ASTM D4239-08 Method B	0.89
	Gross calorific value	MJ/kg Kcal/kg	ASTM D5865-0Ta	20.97 5012
	Net calorific value	MJ/kg Kcal/kg	ASTM D5865-0Ta	19.94 4766

Table 5 Composition of CP® limestone.

Composition	% by weight
$CaCO_3$	99.08 %
$MgCO_3$	0.18 %
Moisture	0.02 %

Table 6 Composition of Sodium Bentonite from Volclay Siam Ltd.

Composition	% by weight
SiO_2	61.16
Al_2O_3	21.20
CoO	0.01
Fe_2O_3	5.09
P_2O_5	0.08
K_2O	0.70
TiO_2	0.19
MgO	2.96
CaO	4.12
Na_2O	1.76
WO_3	0.01
PbO	0.01
BaO	0.04
ZnO	0.01
ZrO_2	0.03
Mn_2O_3	0.03
H_2O	8.44

Table 7 Particle size of raw materials.

Raw material	Particle size		
	average	SD	Range
XK-01(mm)	0.043	0.021	0.110-0.020
Dai coal (mm)	0.115	0.056	0.220-0.020
Limestone (μm)	5.03	1.76	1.63-10.26
Bentonite (μm)	27.64	10.37	8.84-48.09

Effects of the Reduction Time and the Reduction Temperature

The weights of the pellet after the reduction, % Fe Nugget from EDX and % Yield are tabulated in Table 8. Samples No. 1.1 – No.1.7 show the increase in % Fe with increasing reduction temperature and at the reduction time of 50 min, as shown in Figure 2.

The laboratory experiment shows the best reduction time and temperature for making Iron nuggets (% yield more than 90 %, using the mol ratio of mixture C/Fe = 1.72, the mol ratio of Limestone/Al_2O_3+SiO_2 = 0.89 and the mol ratio of Bentonite/Fe = 0.02) belongs to the sample No.1.13, with the reduction time of 20 min, and the reduction temperature of 1425°C.

Table 8 The weight of No. 1.1–1.19 after reduction time 50 min, % Fe Nugget from EDX and % Yield.

No.	Reduction Temperature (°C)	Dried Weight of a pellet (g)	Products (g)		% Fe Nugget from EDX	% Yield
			Nugget	Slag		
1.1	1500	53.09	19.63	6.83	93.09	100.29
1.2	1450	53.09	19.75	5.21	90.20	97.77
1.3	1400	53.37	18.38	11.65	92.15	92.46
1.4	1375	50.73	24.78		-	-
1.5	1350	52.63	27.26		-	-
1.6	1300	53.40	24.00		-	-
1.7	1200	53.09	28.53		-	-
1.8	1450	51.93	16.68	7.11	92.13	86.22
1.9	1450	52.59	18.51	8.24	89.92	92.21
1.10	1450	51.61	17.54	8.70	92.06	91.16
1.11	1450	52.01	17.96	9.57	94.49	95.07
1.12	1425	52.17	17.90	8.77	95.67	95.64
1.13	1425	51.61	17.30	10.47	93.95	91.76
1.14	1425	51.95	17.20	7.16	91.86	88.61
1.15	1425	51.51	26.86		-	-
1.16	1400	52.63	15.92	8.88	91.45	80.60
1.17	1400	52.35	27.11		-	-
1.18	1400	52.43	26.73		-	-
1.19	1375	51.19	26.29		-	-

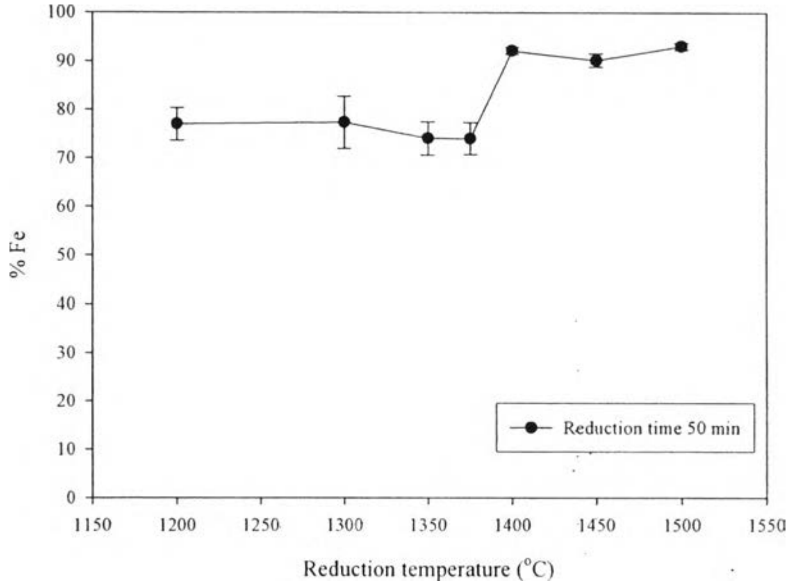


Figure 2 % Fe vs. reduction temperature between samples No.1.1 and No. 1.7.

Effects of the Mol Ratios of the C/Fe and Limestone/Al_2O_3+SiO_2

All pellets were reduced at the reduction temperature 1425°C and at the reduction time of 20 min.

The weights of pellets after the reduction are tabulated in Table 9. Samples No. 2.1 – No. 2.8 show the increase in % Fe with increasing the mol ratio of C/Fe at the reduction temperature of 1425°C and the reduction time of 20 min, as shown in Figure 3.

Table 9 The weight of No. 2.1–3.9 after reduction (1425°C and 20 min), % Fe Nugget from EDX and % Yield.

No.	Dried Weight of 3 pellets (g)	Products (g)		% Fe Nugget from EDX	% Yield
		Nugget	Slag		
2.1	155.24	84.05		-	-
2.2	156.19	82.54		-	-
2.3	159.23	61.92	21.79	91.08	97.73
2.4	149.90	57.60	19.29	93.67	101.17
2.5	150.10	54.72	18.62	92.97	97.01
2.6	153.05	52.51	20.47	93.95	93.92
2.7	152.96	49.20	25.36	94.39	90.02
2.8	156.35	52.69	16.26	93.45	95.00
3.1	156.31	63.07	13.76	89.24	98.42
3.2	157.64	60.82	18.06	71.37	75.80
3.3	157.90	63.56	18.07	81.00	90.41
3.4	158.27	59.92	17.52	94.80	99.90
3.5	163.91	63.88	23.78	89.39	97.92
3.6	159.70	61.71	23.16	80.63	88.26
3.7	159.31	60.25	19.45	89.61	97.73
3.8	160.60	83.19		-	-
3.9	157.36	69.30		-	-

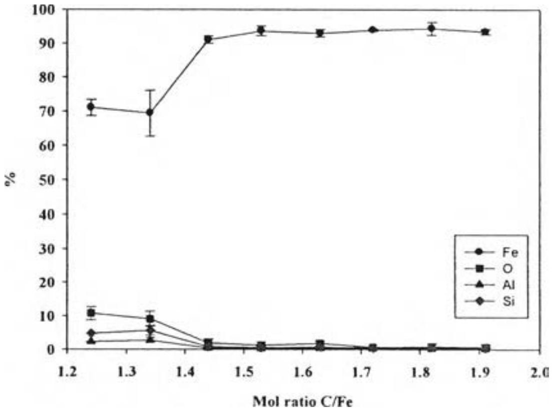


Figure 3 % Element of Iron nugget vs. Mol ratio C/Fe between samples No.2.1 to No. 2.8.

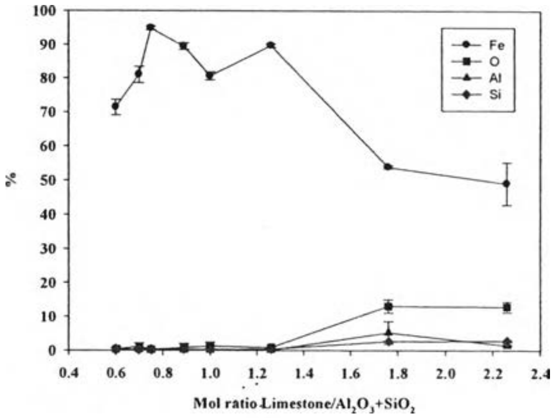
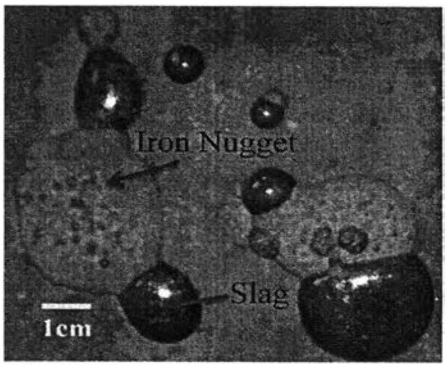


Figure 4 % Element of Iron nugget vs. Mol ratio of Limestone/Al_2O_3+SiO_2 between samples No. 3.2 to No. 3.9.

The reduction temperature 1425°C and the reduction time of 20 min with the minimum mol ratios of mixture C/Fe and Limestone/Al_2O_3+SiO_2 of 1.53 and 0.75, respectively yield the % Fe over 94 % and % Fe yield more than 94 %. Then the sample No. 3.4 is the most suitable because of highest % Fe in Iron nuggets, the highest % yield, and the low Dai coal and Limestone usages.

Table 10 Wt % Element of sample No 3.4.

Element	Wt % Element of pellet No. 3.4		SD	
	Iron nugget	Slag	Iron nugget	Slag
C	2.66	0.00	0.70	0.00
O	0.28	35.06	0.25	3.38
Al	0.08	7.93	0.08	0.41
Si	0.26	18.27	0.13	0.52
K	0.00	1.34	0.00	0.26
Fe	94.80	1.76	0.57	0.76
Zr	0.00	0.00	0.00	0.00
Mn	0.00	0.15	0.00	0.05
Ca	0.12	33.66	0.21	3.40
Ti	0.00	0.59	0.00	0.07
Au	0.00	0.00	0.00	0.00
Cu	0.14	0.00	0.13	0.00
P	0.86	0.00	0.21	0.00
S	0.78	0.49	0.18	0.08
Mg	0.00	0.50	0.00	0.05
Na	0.00	0.25	0.00	0.05
Cl	0.00	0.00	0.00	0.00



No. 3.5 1425°C, 20 min, C/Fe = 1.53/1, Limestone/Al_2O_3+SiO_2 = 0.75 and Bentonite/Fe = 0.02, % Fe = 94 and %Yield = 99, Iron nugget size = 1.88–3.58 cm, Slag size = 048–2.19 cm

Figure 5 The nugget and slag from 3 pellets of sample No. 3.4 after the reduction.

Figure 6 The backscattered SEM image of cross section iron nugget No. 3.4 at reduction temperature 1,425°C and reduction time of 20 min. The lamellar structure represents pearlite, which is alternating layers of α iron and Fe3C, light-gray areas represent cementite (Fe3C) and dark-gray areas represent the iron sulfides. This structure is similar to the white cast iron.

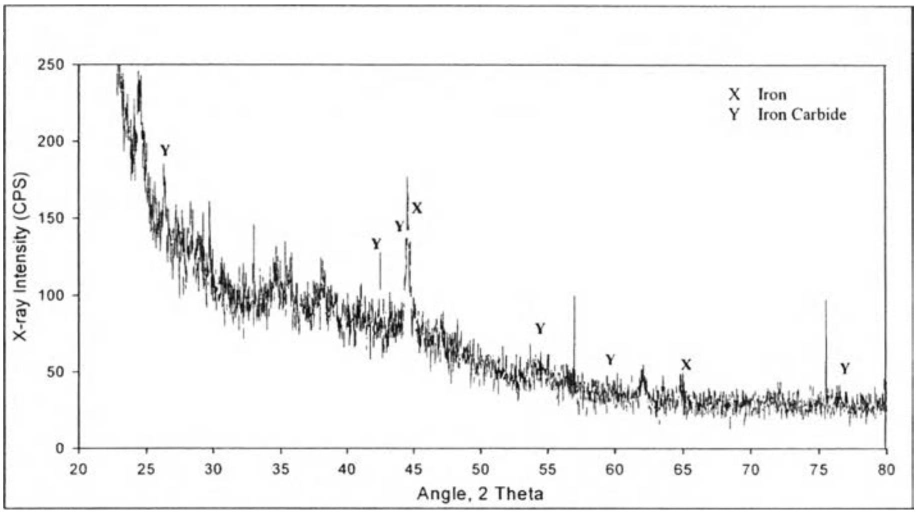
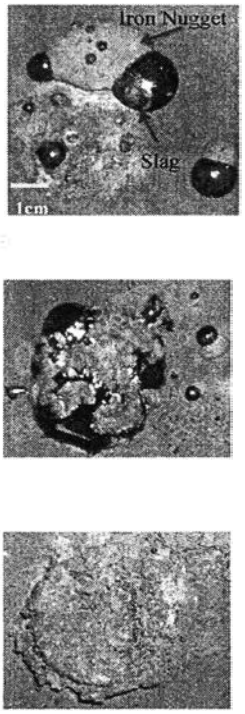


Figure 7 XRD spectrum of Iron nugget No. 3.4

Discussions

The % Yield after reduction of the sample No. 1.1 is over 100 % because another raw materials have iron contents (Dai coal has % Fe = 2.25 and Bentonite has % Fe = 3.56), and errors from the measurements.

The products after the reduction can be classified into 3 types of the phase separation as shown in Figure 6.



No.1.12 1425°C, 30 min
Iron nugget size = 0.56–2.23 cm
Slag size = 0.68–1.48 cm

1. Complete separation:
The Iron was reduced completely. The metal and the slag separate perfectly.

No.1.18 1400°C, 30

2. Partial separation:
The metal and slag separate partially.

No.1.5 1350°C,

3. Direct reduction:
The Iron reduction was not yet complete. The metal and slag are not separated.

Figure 8 Types of separation.

The Figure 2 shows the increase in % Fe with increasing reduction temperature and at the reduction time of 50 min because the reduction of iron oxide is the endothermic reaction. When increasing the mol ratio of C/Fe, % Fe of products increases at the reduction temperature 1425°C and the reduction time of 20 min, as shown in Figure 3. This is because the increasing amount of the reductant in the mixture will increase the extent of the reduction of the iron oxide. Then the % Fe in iron nugget is increased. Figure 4 shows the increasing of % Fe in the products when increasing the mol ratio of Limestone/Al_2O_3+SiO_2. Initial state shows the increase of % Fe. Because, Limestone is converted to calcium oxide and combines with impurity in the iron ore and separate into slag, then % Fe will increase. Further increase in the mol ratio, % Fe is constant because of the complete separation. Further increase in the mol ratio, the % Fe decreases: adding too many moles of Limestone/Al_2O_3+SiO_2, the more energy consumption is required and the reduction becomes incomplete.

Conclusions

The product of the reduction can be classified into three types of phase separation:(1) Complete separation; the iron oxide was reduced completely, the metal and the slag separate perfectly; (2) Partial separation, the metal and the slag separate partially; and (3) Direct reduction, the iron reduction was not yet complete, the metal and slag do not separate. The laboratory experiments show the most suitable conditions for making Iron nugget (over 94 % Fe and % yield more than 94 %) from the low grade iron ore which has 55.99 % iron content and a low grade coal (40% fixed carbon) as the raw materials. The suitable conditions for making Iron nugget, from a pellet which has a diameter of 2.5 cm and 4 cm high, are by using the mol ratios of the mixture as C/Fe = 1.53, Limestone/Al_2O_3+SiO_2 = 0.75, and Bentonite/Fe = 0.02/1 with the reduction temperature of 1425°C and at the reduction time of 20 min.

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