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RESEARCH ON SELF-REDUCTION OF IRON-BEARING DUST FOR IRON NUGGETS[1]

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Abstract
A new pig iron making process using iron-bearing dust containing coal as reducing agent has been studied. The pellets were heated rapidly in nitrogen at furnace temperature between 1,350°C and 1,400°C.Then the pellets were token out from the furnace and cooled to the room temperature after cooling to 700°C in the furnace. The result shows that the pellets spontaneously disperse when pellets basicity is more than 1.8. The best inner C/O mole ratio and basicity for iron and slag separating completely is 1.1and 2.0 respectively. Under the condition, iron yield was more than 95%, iron nuggets within 5-20mm was more than 80% and desulphurization rate was more than 85% when the reduction temperature is more than 1,350°C.
Key words: Iron-bearing dust; Pellets; Self-reduction; Iron nuggets.

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1 INTRODUCTION

With the rapid development of steel industry in China，recycle and comprehensive utilization of dust in iron and steel plant receives much more concerns yet. Generally speaking, dust amount is 8-15 percent of steel output[1]. Million tons of dust was generated in domestic every year. Well process and recycle them can give tremendous economic and environmental benefit.

Nowadays iron-bearing dust is generally processed in sintering with recycling use, leading to Pb, Zn, K and Na enrichment, harming the production of blast furnace. Coal-based direct reduction using coal as reducing agent is suitable for processing iron-bearing dust. With strong adaptability to raw material and flexible operation, RHF process has been developing quickly in recent years in China[2,3]. While achieving high quality DRI with lower Cu, Co, Cr compared with scrap for EAF, RHF process also removed harmful elements zinc, lead etc. The shortcoming of RHF process is that DRI includes relatively high S content, leads to slag content of EAF increasing and electrode consumption.

To solve this problem, the installation of a submerged arc furnace (SAF) after the DRI process has been attempted[4]. This method is able to supply slag free hot metal to EAF, but requires a large investment for the SAF and has the disadvantage of high power consumption.

The naissance of ITmk3[5] process has broke through the characteristics of direct reduction product in traditionally. The pellets are melted in the last zone of the rotary hearth furnace hearth to produce a premium quality pig iron product with a slag by-product. But high grade iron concentrate was required in ITmk3 process, as well as problems of melting acid gangue bonding with the lining.

Therefore this paper emphasizes to the influencing factors of pellet self-reduction, change direct reduction products from DRI with acid gangue to iron nuggets, control S,P content in the iron nuggets at the same time. Provide the foundation for one step reduction obtaining iron nuggets and industrial processing iron-bearing dust.

2 EXPERIMENTAL

2.1 Experimental Principle

The reduction of pellets containing carbon is called self-reduction. Since the intimate contact of oxide iron and carbon, CO_2 reducing from the oxide iron（$Fe_2O_3 + CO = 2Fe + CO_2$ and $FeO + CO = Fe + CO_2$）could conversion to CO in-situ and then taking part in reduction reaction immediately. Compared with ordinary coal-based direct reduction it is showed superior in kinetics conditions, fast reaction rate and short reaction time. The pellets spontaneously disperse since the phase transition of $2CaO{\cdot}SiO_2$. Iron and slag separation is realized.

2.2 Materials and Sample Preparation

The iron-bearing dust used in this study included cast house ash, gas ash, steelmaking sludge and mill scale. Anthracite was used as reducing agent. The additive was hydrated lime. Chemical composition and particle size was show in table 1 and 2.The particle size of mill scale smaller than 100 mesh taken 56 percent and anthracite smaller than 200 mesh taken 80 percent respectively.

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Table 1. Chemical composition (weight %) of iron bearing dust

Name	TFe	FeO	Fe_2O_3	CaO	SiO_2	Al_2O_3	MgO	K_2O	Na_2O	Pb	Zn	P	S	C
steelmaking sludge	46.10	58.20	1.19	16.13	3.09	0.59	4.25	0.22	0.98	0.007	0.07	0.095	0.16	4.56
cast house ash	62.44	11.68	76.22	0.50	1.97	0.83	0.14	0.78	0.16	0.006	0.11	0.080	0.29	4.30
gas ash	30.87	4.88	38.68	2.50	5.86	3.15	0.64	0.35	0.15	0.011	0.064	0.052	0.17	34.25
mill scale.	71.61	53.63	42.71	0.47	0.51	0.13	0.01	-	-	-	-	0.008	0.01	-
anthracite	1.47	1.89	-	1.45	2.49	1.29	0.23	0.077	0.12	0.002	0.003	0.011	0.27	81.46
hydrated lime	-	-	-	68.48	1.34	0.65	0.26	-	-	-	-	0.003	0.10	-

Anthracite: Ad 8.06% , Vd 10.48%

Table 2. Particle size of iron bearing dust

NO.	Particle size	Mesh mm	+35 +0.5	35~60 0.5~0.25	60~80 0.25~0.2	80~120 0.2~0.125	120~160 0.125~0.098	160~200 0.098~0.074	-200 -0.074
1	steelmaking sludge	%	11.5	19.92	7.62	25.13	9.27	16.33	10.22
2	cast house ash	%	17.91	7.2	3.51	7.4	3.79	5.31	54.88
3	gas ash	%	17.59	20.8	6.39	20.2	10.47	14.64	9.92

The carbon content in the pellets was expressed by C/O mole ratio in this paper. The consumed carbon which iron oxides were directly reduced to iron completely in pellets was expressed as C/O=1. The designed C/O mole ratio is 1.1-1.2. 2% CaF_2 was added in the raw materials for it is benefit to the separation of iron and slag. To assure forming $2CaO \cdot SiO_2$, the designed slag composition should be located in $2CaO \cdot SiO_2$ phase region in phase diagram of $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO$. Means that when Al_2O_3 was 10 mass pct., CaO should more than 50 mass pct., SiO_2 should less than 40 mass pct. and MgO should less than 14 mass pct. Meanwhile basicity (R) should be controlled between 1.8 and 2.2. The designed raw material ratio based on mentioned above show in table 3. And their chemical composition show in table 4. The correlated theoretical composition of slag samples was marked in phase diagram as show in fig 1. All slag composition were located in $2CaO \cdot SiO_2$ phase region.

Table 3. raw material ratio of samples

No.	steelmaking sludge	cast house ash	gas ash	Mill scale	anthracite	hydrated lime	CaF2	C/O	R
C1.1R1.8	13.92	41.77	27.84	9.28	3.86	3.33	2	1.1	1.8
C1.1R2.0	13.79	41.38	27.59	9.20	3.82	4.22	2	1.1	2.0
C1.1R2.2	13.67	41.00	27.33	9.11	3.78	5.11	2	1.1	2.2
C1.2R1.8	13.68	41.04	27.36	9.12	5.45	3.35	2	1.2	1.8
C1.2R2.0	13.55	40.66	27.11	9.04	5.40	4.24	2	1.2	2.0

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Table 4. Chemical composition (weight %)of samples

No.	TFe	FeO	Fe_2O_3	CaO	SiO_2	Al_2O_3	MgO	K_2O	Na_2O	Pb	Zn	P	S	C
C1.1R1.8	47.80	19.40	46.73	5.53	3.07	1.39	0.85	0.46	0.25	0.007	0.074	0.062	0.21	15.11
C1.1R2.0	47.37	19.22	46.30	6.11	3.06	1.38	0.84	0.45	0.25	0.007	0.073	0.062	0.20	14.97
C1.1R2.2	46.92	19.04	45.87	6.69	3.04	1.38	0.84	0.45	0.25	0.006	0.072	0.061	0.20	14.83
C1.2R1.8	46.99	19.10	45.92	5.51	3.06	1.39	0.84	0.45	0.25	0.007	0.072	0.061	0.21	16.20
C1.2R2.0	46.56	18.92	45.50	6.09	3.05	1.38	0.83	0.45	0.25	0.006	0.072	0.061	0.21	16.05

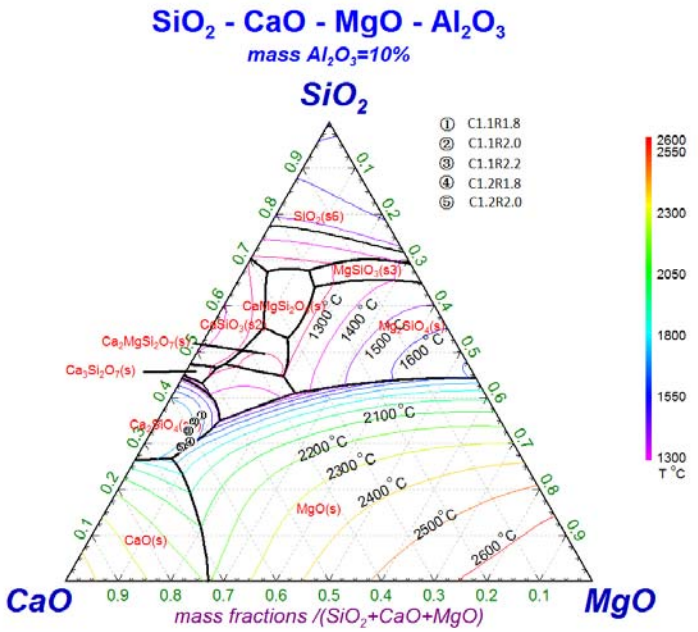

Fig 1. Location of theoretical composition of slag in phase diagram.

2.3 Experimental Procedure and Equipment

Mixing and drying kinds of raw materials then passing through 1mm sieve twice. To assure uniform mixing 12%-15% water or sodium silicate was added for wetting the raw material. Then pass through 2mm sieve twice to scatter the agglomerate and make the internal raw material uniform mixed. At last, the uniform mixture was compacted to φ20×25mm cylindrical specimens using apparatus as show in fig 2(a). Specimens were placed in the dryer after drying to constant weight.

The experiment was undertaken in high-temperature carbon tube furnace, the facility was show in fig 2(b). Power of carbon tube furnace is 25KVA, inner diameter of heat-generating elements is 70mm. The height of the isothermal segment is 50mm. And heating rate is 100-150□/min. N_2 was blow in during experiment to protect carbon tube from oxidation.

The pellets were heated rapidly in nitrogen at furnace. Isothermal for 10 min at the temperature predetermined. Reduction, solid reaction, carburization aggregation of iron was carried on under the reduction temperature. The pellets were cooling to 700°C in the furnace, then token out from the furnace and cooled to the room temperature.

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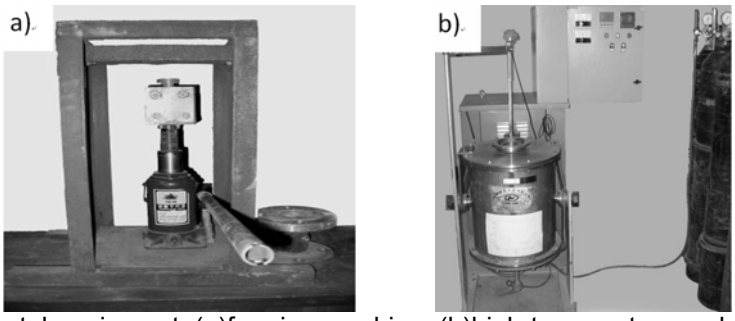


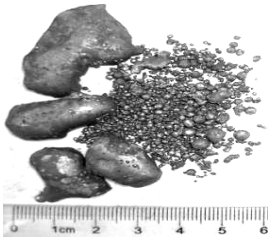
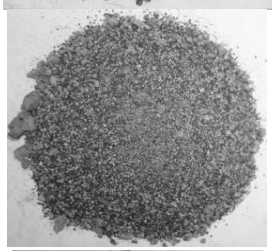
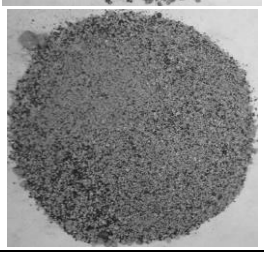
Fig 2. Experimental equipment. (a)forming machine, (b)high-temperature carbon tube furnace.

3 EXPERIMENTAL RESULTS AND ANALYSIS

3.1 The Influence of Slag Basicity, Inner C/O Mole Ratio and Reduction Temperature on Separation of Iron and Slag

Cooled samples were passed through 0.125mm sieve to separated iron nuggets from slag. The separated iron nuggets and slag were show in table 5.

Table 5. Morphology of separated iron nuggets and slag after reduction

No.	Ratio	Nuggets	Slag	Temperature.
1	II-C1.1R1.8		Separation of iron and nuggets were not thorough	1400℃
2	II-C1.1R2.0			1400℃
3	II-C1.1R2.0			1350℃
4	II-C1.1R2.2			1400℃

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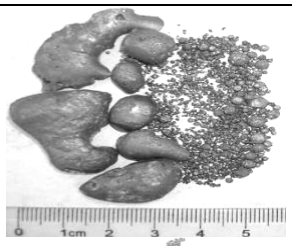
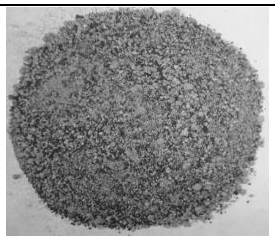
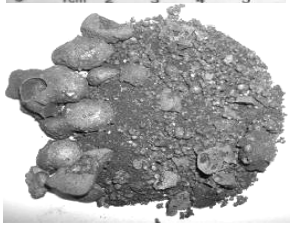
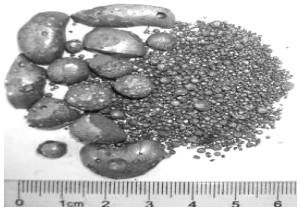
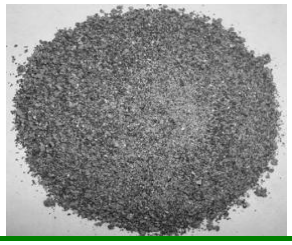
5	II-C1.1R2.2			1350℃
6	II-C1.2R1.8		Separation of iron and nuggets were not thorough	1400℃
7	II-C1.2R2.0			1400℃

Table 5 reveals that the separation of iron and slag was not thorough when slag basicity was 1.8. The range of reasonable slag basicity was 2.0-2.2. Slag composition was controlled in $2CaO{\cdot}SiO_2$ phase region. $\alpha-2CaO\cdot SiO_2$ with high melting point was produced by solid reaction between CaO and SiO_2 at high temperature. Crystal structure of $2CaO{\cdot}SiO_2$ transformed from $\alpha-2CaO\cdot SiO_2$ to $\alpha'-2CaO\cdot SiO_2$ and $\beta-2CaO\cdot SiO_2$ during cooling, then transformed to $\gamma-2CaO\cdot SiO_2$ when temperature below 670℃, accompanied by volume expansion of 10%. The natural degradation of slag realized the separation of iron and slag. The reduced iron at high temperature has accumulated to dense metal particles. So even under oxidizing atmosphere, reoxidation was not happened to assure high metallization rate.

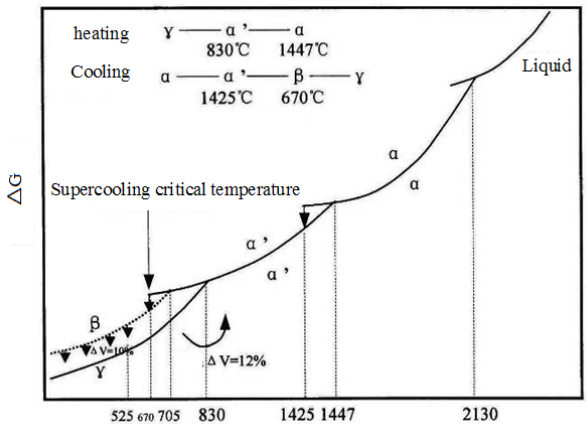


Fig 3. variant of calcium orthosilicate.

The controlled inner C/O mole ratio was 1.1-1.2, the melting point of reduced metal decreased through carburization and the reduced iron accumulated to metal particles by high temperature diffusion. Either high or low inner C/O mole ratio was not benefit to accumulation of iron. When C/O mole ratio was too low, carbon in the pellets was mainly consumed for iron reduction, leading to low carburization of reduced iron and

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high droplet temperature. When C/O mole ratio was too high, one hand the contact area between Fe and C was decreased whereas, carburization condition was deteriorated and carburization was depressed. On the other hand, residual carbon retained in pellets prevented from accumulating of iron and slag, not benefit to the aggregation and growth of iron nuggets.

Iron nuggets were pass through 5mm sieve to grade. The proportion of iron nuggets bigger than 5mm was show in fig 4. The mass percent of iron nuggets bigger than 5mm can over 80% stably when inner C/O mole ratio was 1.1, basicity was 2.0-2.2 and reduction temperature was higher than 1350°C.

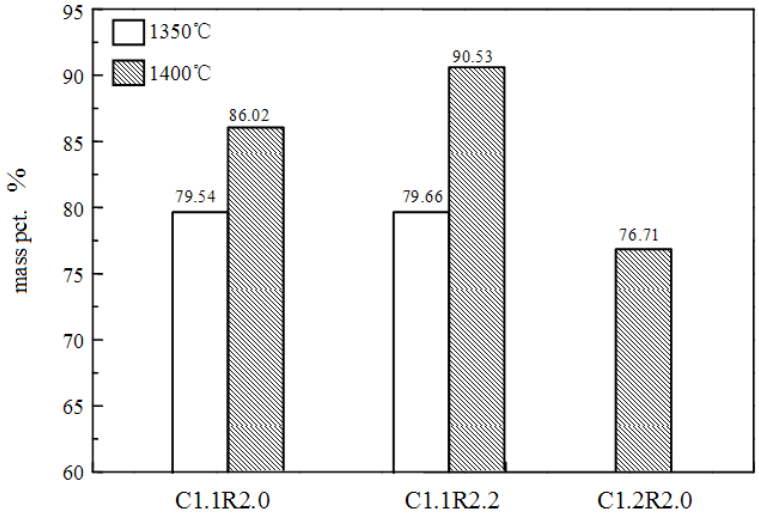

Fig 4. Influence of reduction temperature on the size of iron nuggets.

3.2 Metallization Rate, Dephosphorization and Desulphurization Rate

During self-reduction of the pellets, P_2O_5 in raw materials can be reduced to gaseous P_2. Partial of it can be absorbed by sponge iron then remained in iron nuggets finally. The reactions were show as follows:

$$2Ca_3P_2O_8 + 3SiO_2 + 10C = 3Ca_2SiO_4 + 2P_2 + 10CO$$

$$2Ca_3P_2O_8 + 3SiO_2 + 10C = 3Ca_2SiO_4 + 4[P]_{nuggets} + 10CO$$

When the pellets has higher CaO, the reactions above were inhibited. P which was not reduced was removed through the separation of iron and slag. So the dephosphorization rate included two parts. P in apatite that was not reduced and P_2 escaped from carbon content pellets as the form of vapor.

At the same time during self-reduction of the pellets, desulfurization reaction as follows occurred accompanied by carbon gasification:

- FeO + C = Fe + CO
- FeO + CO = Fe + CO2
- $CO_2 + C = 2CO$
- $1/2S_2 + CO = COS$
- $FeS + CO = Fe + COS$

COS as the products of desulfurization reaction mentioned above would escape from pellets with CO. While CaO existed in the pellets, COS can be reacted with it producing CaS: $CaO + COS = CaS + CO_2$.

S in slag would be removed with the separation of iron and slag. So the total desulfurization rate included the removed S content in the form of COS and CaS.

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Grade the iron nuggets obtained according to 0.125-5mm and 5-20mm. TFe and P content in the iron nuggets was analyzed by ICP analyzer. C and S content in the iron nuggets was analyzed by infrared carbon and sulfur analyzer. Chemical composition of iron nuggets obtained show in table 6.

Table 6. Chemical composition of iron nuggets

No.	Ratio	grade	TFe	P	S	C
1	II-C1.1R1.8-1400	Separation of iron and nuggets were not thorough				
2	II-C1.1R2.0-1400	>5mm	94.21	0.103	0.0054	4.86
		<5mm	88.33	0.086	0.0167	5.75
3	II-C1.1R2.0-1350	>5mm	91.01	0.106	0.0131	4.45
		<5mm	86.25	0.091	0.0142	4.62
4	II-C1.1R2.2-1400	>5mm	94.02	0.090	0.0043	4.80
		<5mm	93.97	0.118	0.0242	5.00
5	II-C1.1R2.2-1350	>5mm	94.40	0.101	0.0187	3.35
		<5mm	93.14	0.102	0.0211	4.71
6	II-C1.2R1.8-1400	Separation of iron and nuggets were not thorough				
7	II-C1.2R2.0-1400	>5mm	93.39	0.190	0.0042	5.27
		<5mm	87.80	0.099	0.0186	4.98

Yield of metal, dephosphorization and desulphurization rate calculated show in table 7. Iron yield was more than 95% when inner C/O mole ratio is 1.1and basicity of slag phase is within 2.0-2.2.

Table7. Yield of metal, dephosphorization and desulphurization rate(%)

No.	Ratio	η_{Fe}	$\Delta\eta_P$	$\Delta\eta_S$	Carbon content
1	II-C1.1R1.8-1400	Separation of iron and nuggets were not thorough			
2	II-C1.1R2.0-1400	97.89	19.41	98.64	4.98
3	II-C1.1R2.0-1350	92.35	19.34	96.76	4.49
4	II-C1.1R2.2-1400	93.11	29.42	98.55	4.82
5	II-C1.1R2.2-1350	90.18	25.43	95.68	3.62
6	II-C1.2R1.8-1400	Separation of iron and nuggets were not thorough			
7	II-C1.2R2.0-1400	91.67	28.27	98.33	5.21

4 CONCLUSION

High temperature self-reduction experiment was carried on the pellets which used cast house ash, gas ash, steelmaking sludge and millscale as raw materials, anthracite as reductant and CaF_2 as additive. Hydrated lime was added to adjust the basicity of slag. The conclusions drawn are as follows:
2CaO·SiO2 was completely formed by solid reaction in High temperature self-reduction experiment when the slag basicity higher than 1.8, and reduction products natural separated completely after cooling.

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The mass ratio of iron nuggets bigger than 5mm can be over 80% when the temperature was 1350°C-1400°C. The controlled inner C/O mole ratio and slag basicity should be 1.1-1.2 and 2.0-2.2. The recommended inner C/O mole ratio and slag basicity is 1.1 and 2.0,under this condition, iron yield is more than 95%, iron nuggets within 5-20mm is more than 80%, desulphurization rate is more than 85% when the reduction temperature is more than 1350°C.

Pellets with high basicity have excellent desulfurization conditions. It also has a certain capability of dephosphorization as the inhibition of high basicity slag on the reduction of P_2O_5 by carbon. Under all ratio and conditions, the total desulfurization rate is 92%~98%.

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