

Effect of Volatile Matter Content of Coal on Carbothermic Reduction of Ore / Coal Composite Pellets Packed in a Tall Bed

TSUNG-YEN HUANG, SHIH-HSIEN LIU and GANG-HERNG SHIAU

*Iron & Steel Research Development Department
China Steel Corporation*

At present, the ironmaking route via the carbothermic reduction idea based on ore/coal composite pellets packed in a tall bed in a hearth furnace is one of the most promising processes. Carbothermic reduction has the following characteristics: (a) Coal-base. (b) Without coke making and ore sintering. (c) Low coal rate, which are not only helpful to broaden the selection of raw materials but also a cleaner approach to the ironmaking process. In this study, we focused on the effects of Volatile Matter (VM) content of the coal properties in ore/ coal composite pellets. The temperature variation at the bottom of the pellet bed during whole reduction period was recorded showing the ranking for the temperature rising rate at the bottom of the pellet bed with green balls with 33% VM coal, with a mixture of 33% VM plus 5% VM coal and with 5% VM coal. It was indicated that a pellet composed of higher amounts of VM in coal promotes the degree of DRI shrinkage percentage, causing a higher heat transfer rate from the top to the bottom of the pellet bed. The chemical composition for the bulk and for the specific zone of the DRI sample was analyzed, respectively. As using 33% VM coal as a reductant, the metallization of the DRI sample is not only high but also lower difference across the pellet bed, ranging from 95 to 92%. On the other hand, using 5% VM coal as a reductant, high iron productivity was obtained. As well as the carbon utilization of 5% VM coal is relatively higher than that of 33% VM coal for carbothermic reduction. The results are expected to be a criterion of the coal selection and to be preliminary understanding on the thermal-chemical behavior of the carbothermic reduction for ore/coal composite pellets packed in a tall bed.

Keywords: Carbothermic reduction, Composite pellet, Direct Reduced Iron (DRI), Tall pellet bed

1. INTRODUCTION

The current state of the global steel industry, with respect to ironmaking, is based on blast furnace technology. Due to its productivity and energy efficiency, the blast furnace has been the most important ironmaking reactor. However, researchers in industry are constantly developing alternative ironmaking processes to replace the blast furnace. The reasons are that the blast furnace demands strict quality control of raw materials and results in environmental issues. Moreover, in the last decade, the high-grade iron ore and coking coal have become increasingly in short supply and costly. Meanwhile, the environmental regulations for the ironmaking process are getting stricter. Of all the favored non-blast furnace ironmaking ideas at the present time, the carbothermic reduction idea based on ore/coal composite pellets packed in a tall bed in a hearth furnace is one of the most promising processes⁽¹⁾. Carbothermic reduction also has the following characteristics: (a) Coal-base. (b) Without coke making and ore sintering. (c) Low coal rate, which are not only helpful to broaden the selection

of raw materials but also a cleaner approach to the ironmaking process.

On the basis of carbothermic reduction, the Rotary Hearth Furnace (RHF) reactor has been well developed⁽²⁾. However, the RHF reactor was used to process the waste oxide which was generated from the steel industry. As well as the metallization percentage of Direct Reduced Iron (DRI) produced from RHF is normally at the range of 60 to 70%. Recently, Lu and Huang proposed a new ironmaking process also base on carbothermic reduction named Paired Straight Hearth (PSH) furnace^(3,4). Ore/coal composite pellets packed in a tall bed in the hearth furnace with a high flame temperature (1600 to 1650°C) are the main processing characteristics of PSH. Comparing to RHF, the PSH process is anticipated to obtain the high metallization percentage DRI, to improve the productivity of metal iron, to increase the fuel efficiency of coal, and to well control carbon content in DRI. Lu and Huang⁽⁵⁾ also reported the systematically experimental results based on the raw materials of some specific iron ore concentrates, waste oxides and coals, showing that degree of metallization

of DRI reached 95% and the iron productivity was nearly 100 kg-Fe/m²h over three fold of RHF's productivity. The main factors to influence the behavior of carbothermic reduction include green ball properties, pellet bed conditions and heating conditions. For the effects of green ball properties, A. Tejasukmana et al⁽⁶⁾ conducted three kinds of reductants, graphite, coke and coconut charcoal, with different reactivity to explore the extent of reduction and the shrinkage of DRI. It was found that the extent of reduction and degree of shrinkage of pellets made with coconut charcoal, which is generally more reactive than coke and graphite, were higher than in the case of pellets made with coke but lower than in the case of pellets made with graphite. However, because the experiments were based on a single pellet, the results are an important reference for the behavior of carbothermic reduction but it cannot directly apply on the reduction behavior in a tall pellet bed.

To develop a high performance ironmaking process of carbothermic reduction at China Steel (CSC), in the early stages of the study, we had to conduct a series of experiments with the available raw materials to understand the reduction characteristics. Although the raw materials of iron ore and coal are both important to affect the reduction behavior, in this study we focused on the effects of coal type. The results are expected to obtain a criterion of coal selection and to be preliminary understanding on the thermal-chemical behavior of the carbothermic reduction for ore/coal composite pellets packed in a tall bed.

2. EXPERIMENTAL

2.1 Raw materials

The iron oxide used for this study was the hot strip mill scale from Chung Hung Steel. The particle size of mill scale is 100% under 100 μ m. The chemical composition of the mill scale is shown in Table 1, which indicated that the majority was iron oxide with a small amount of impurity. Mill scale also accompanied with some carbon and oil. Note that the amount of 56.8% FeO and 34.6% Fe₂O₃ chemical composition were converted to 41.2% Wustite FeO and 50.3% Magnetite Fe₃O₄. Table 2 shows the chemical composition of reductants, coal A and coal B, which is both recognized as non-coking coal. The general difference was that the Volatile Matter (VM) of coal A was much higher than that of coal B. Usually, coal A is called high volatile coal and coal B is called anthracite (hard coal), respectively. Before pelletizing, the coals were both crushed and ground to 100% under 250 μ m. The stoichiometric atomic ratio of Carbon/Oxygen (C/O) for green ball preparation was assumed as 1.1 where the carbon was total carbon in coal and the oxygen stood for reducible oxygen in iron oxide. Moreover, 1% of bentonite given the chemical composition in Table 3 was added into the mixture of coal/iron oxide as binder for assistance of forming the pellet. Three kinds of green balls with the size of 15 to 16 mm were made by using a disk pelletizer. Table 4 shows the sample conditions for carbothermic reduction. The samples are inherent with the different amount of Theoretical Maximum Weight Loss percentage (TMWL) and the weight of loading at the same packing volume because of the pellet density.

Table 1 Chemical composition of iron source (mass %)

Constituents	T.Fe	FeO	Fe ₂ O ₃	M.Fe	C	CaO	Al ₂ O ₃	SiO ₂	MgO	S	P	Oil
Content	68.41	56.77	34.64	0.18	4.22	0.26	0.07	0.25	N.D.	0.11	0.03	2.26

Table 2 Chemical composition of coal (mass %)

	Proximate analysis (ad)				Ultimate analysis (ad)					
	H ₂ O	VM	Ash	FC	T.C.	H	S	N	O	
Coal A	1.04	33.20	7.94	57.82	74.08	4.55	0.52	1.30	10.56	
Coal B	2.42	5.21	13.92	78.45	80.66	0.87	0.22	0.08	N.D.	
Ash composition (in ash)										
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	MnO
Coal A	66.76	26.01	3.29	1.32	1.05	0.67	0.75	0.93	0.57	0.04
Coal B	62.32	24.66	5.19	1.15	1.11	0.83	1.42	4.82	0.42	0.11

Table 3 Chemical composition of binder (mass %)

Constituents	CaO	MgO	Al ₂ O ₃	SiO ₂
Content	2.48	1.11	11.16	67.99

2.2 Experimental method

The carbothermic reduction experiment was performed in an electric resistance furnace, its picture and schematic diagram shown as Fig.1. The hearth can be moved out from the hot zone to allow the crucible with the pellets to be loaded. For the commercial hearth furnace, the heat source is usually provided by the radiation of firing and the heat is mainly transmitted from the firing and the heated refractory to the top of the pellet bed, and then to the bottom of the pellet bed. Therefore, to ensure the heat transferred from the top of the pellet bed to the bottom of the pellet bed, the siding of the crucible was covered by insulating brick with a 80 mm thickness. The bottom of the crucible was open. The green balls were held inside the crucible by using a metal screen mounted onto the inside wall of the crucible. In this way, the trial sample here was reasonable enough to represent the middle part of a reaction sample of a commercial hearth furnace. Figure 2 shows the experimental crucible. The loading diameter and height of pellet bed was 80 mm and 100 to 110 mm, respectively.

The experimental procedure are as follows: (a) Heated the furnace to 1200°C and then kept at 1200°C for 30 min for stabilizing the furnace temperature. (b) Moved out the hearth and load the crucible with green balls onto the hearth. (c) Moved the hearth with sample into hot zone of furnace. (d) The furnace was then heated to 1500°C for reduction. The total reduction time was 70 min. (e) Moved out the hearth and a hood flowing with sufficient nitrogen immediately covered the crucible to quickly cool down the DRI. During the reduction period, nitrogen was blown into the furnace to maintain the inert atmosphere and a thermocouple was placed in the bottom of the pellet bed to record the temperature variation.

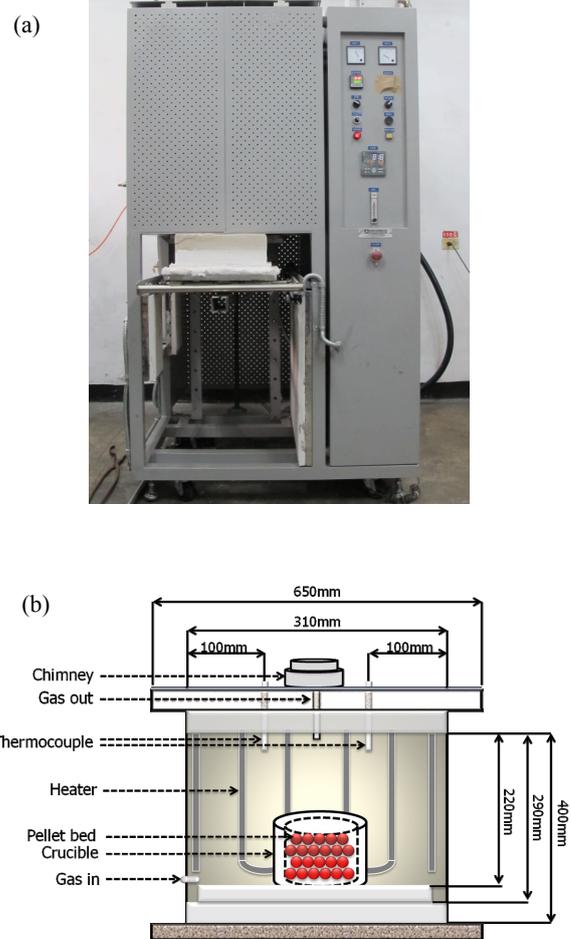


Fig.1. (a) The picture and (b) the schematic diagram of the experimental apparatus.

2.3 DRI sampling and analysis

After a cooling period, the bed of DRI was divided into three portions, top, middle and bottom. The top portion was taken from the first two layer of DRI bed; the bottom portion was taken from the last layer of DRI bed; finally, the middle portion was the remaining layers.

Table 4 Sample conditions for carbothermic reduction in tall pellet bed

Sample name	Coal	Ore	C/O	Bed height (mm)	Loading (g)	TMWL (%)
Pellet A	Coal A				529.2	39.6
Pellet B	50% Coal A + 50% Coal B	Mill scale	1.1	100~110	542.4	38.0
Pellet C	Coal B				642.8	34.8

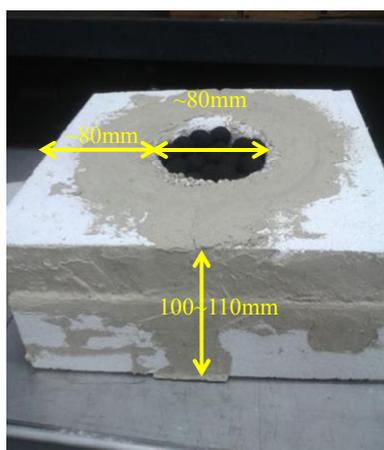


Fig.2. The picture of crucible loading with the green balls.

2.3.1 DRI shrinkage percentage

Every single DRI pellet was detached from the pellet bed to measure its diameter. The degree of DRI shrinkage was calculated as follows (Eq.1).

$$\text{Shrinkage \%} = \frac{\text{Diameter of green ball} - \text{Diameter of DRI}}{\text{Diameter of green ball}} \times 100\%$$

..... (1)

2.3.2 DCR percentage (Degree of Completed Reduction)

The pellets were weighted before and after reduction to estimate the DCR % (Eq.2).

$$\text{DCR\%} = \frac{\text{Weight Loss\%}}{\text{Theoretical Maximum Weight Loss\%}} \times 100\%$$

..... (2)

The TMWL here was the combined weight of all removable oxygen, carbon, hydrogen and matter in the green balls.

2.3.3 DRI metallization percentage

The DRI was ground down to -200 mesh powder for chemical analysis to determine the contents of total iron, metallic iron, FeO and residual carbon. The metallization % was calculated as follows (Eq.3).

$$\text{Metallization \%} = \frac{\text{M.Fe of DRI}}{\text{T.Fe of DRI}} \times 100\%$$

..... (3)

2.3.4 Metallic iron productivity (kg-Fe)/(h*m²)

The metallic iron productivity was calculated as follows (Eq.4).

$$\text{Productivity} = \frac{\text{M. Fe weight of DRI}}{\text{Reaction time} \times \text{Bed area}}$$

..... (4)

2.3.5 Scanning Electron Microscopy (SEM)

A cross section of the DRI was mounted in resin. After grinding and polishing, the observation side of the DRI was coated with a layer of carbon to carry out the SEM analysis. The Joel 6300 equipped with Energy Dispersive X-Ray analysis (EDX) was used for microstructure observation and the X-ray microanalysis.

3. RESULTS AND DISCUSSION

3.1 Temperature variation

Figure 3 shows the temperature variation at the bottom of the pellet bed during the whole reduction period. For the first 50 min of the reduction period, the temperature variation of the three samples nearly overlapped. However, in the last 20 min of the reduction period, the temperature increased at different rates. The ranking for the temperature increase is sample A, sample B and sample C, respectively, implying that the heat transfer rate from the top of the bed to the bottom of the bed is significantly influenced by the coal type mixed in the green pellets.

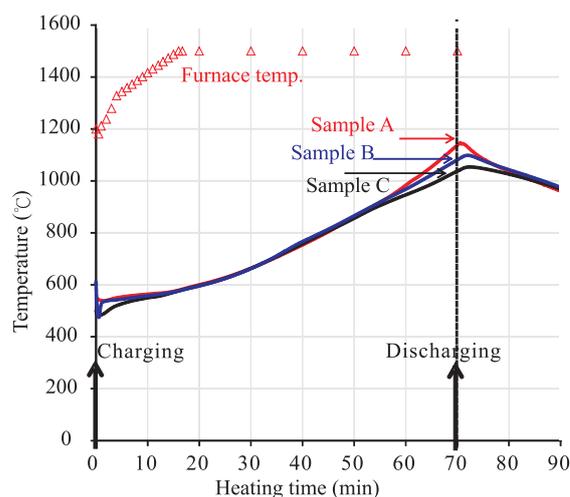


Fig.3. Temperature variation in the bottom of pellet bed.

Generally speaking, the heat transfer dominates the efficiency of reduction reaction in the ironmaking process. Especially in carbothermic reduction of pellets

packed in a tall bed, the radiation directly transmits heat to the pellet bed for the heat consumption of reduction. As the top layer of pellets complete the reduction, the DRI with highly metalized pellets shrinks because of porous iron sintering. The behavior of DRI shrinkage results in the expansion of the heating area and the decrease of the shielding area between pellets to the lower layers. Therefore, the degree of DRI shrinkage significantly affects the heat transfer rate from top to bottom. The 22.4% shrinkage of sample A is higher than that of sample B and C given in Table 5. According to the results combining both of the temperature variation and DRI shrinkages percentage, it is suggested that pellets composed of higher amounts of VM in coal causes the higher heat transfer rate in the pellet bed.

3.2 DRI appearance and SEM analysis

Figure 4 shows pictures of the DRI samples with (a) top view, (b) bottom view and (c) side view. Some of the DRI on the top layer are hollow, which was supposedly caused by the metallurgical competition between the reduction rate and slag formation rate. Sample C has a larger number of hollow DRIs compared to other samples on the top layer. Furthermore, a crack in the top layer of sample A DRI was observed, which was due to a trace of swelling in the early stages of reduction. Although the appearance of the DRI on the top layer varies, it is not a critical issue to affect the metallization percentage of DRI. In the side view of the DRI, it shows that the bulk volume of sample C is the largest one and that of sample A is the smallest, indi-

cating that the shrinkage percentage of sample A is higher than that of the other samples. The specific portion and whole sample shrinkage percentage averaged by every individual DRI were also measured and plotted as shown in Fig.5 and the detailed data shown in Table 5. It displays the shrinkage percentage of the whole sample increased with increasing the addition of coal A in the green ball. Usually, because the heating and reduction direction are both from top to bottom, the shrinkage percentage of the bottom DRI is much less than that of the top, illustrated as measured data of samples B and C. However, in sample A, the shrinkage percentage of the bottom DRI was as much the same as that of the middle and top DRI. This was because the pellet composed of a higher VM in the coal which is inherent with lower density green balls. And when approaching the end of reduction, the individual DRI shrinkage percentage of sample A is thus theoretically the largest one through all of the pellet beds.

Figure 6 shows the cross section SEM images and EDX analysis of sample A of the top layer DRI. Figure 6(a) is a low magnification image taken near the surface of the DRI, showing the porous structure of the DRI. Figure 6(b) is a middle magnification image enlarged from the marked area in Fig.6(a). Figure 6(c) is a zoomed in image of Figure 6(b) showing the edge of the DRI surface. The EDX analysis data in Fig.6(d) indicates that the bright area is iron and the gray area is slag. Note that there is only a small amount of oxygen on the edge of DRI surface. It is suggested nearly no re-oxidation happened on the DRI surface.

Table 5 The analysis results including Shrinkage %, DCR %, Metallization wt%, Iron Productivity and residual Carbon and FeO wt% of DRI

Sample	Sampling position	Shrinkage (%)		DCR (%)	Metallization (%)		Productivity (kg-Fe)/(h*m ²)	C (%)	FeO (%)
		Individual	Average		Individual	Average			
Sample A	Top	22.60			92.00			0.05	9.17
	Mid.	23.10	22.40	98.8	94.10	93.70	46.65	0.18	6.83
	Bot.	21.00			95.30			1.58	5.36
Sample B	Top	17.70			92.50			0.21	8.68
	Mid.	20.40	17.60	97.7	94.60	91.10	46.5	1.29	6.14
	Bot.	13.90			85.40			4.66	15.62
Sample C	Top	20.50			97.10			0.97	2.95
	Mid.	21.80	15.50	91.1	95.10	91.90	57.56	3.06	4.79
	Bot.	15.70			81.10			6.84	19.1

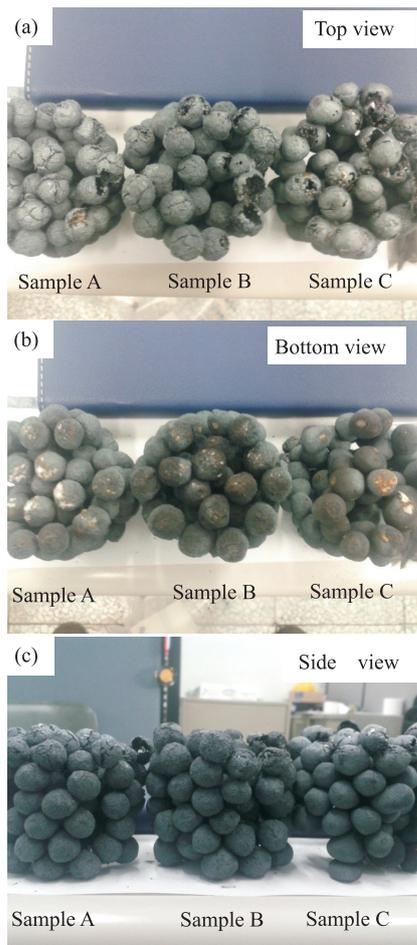


Fig.4. DRI pictures of samples with (a) top view, (b) bottom view and (c) side view.

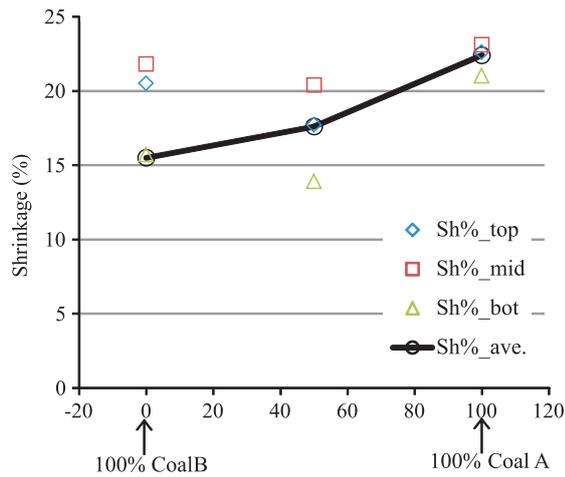
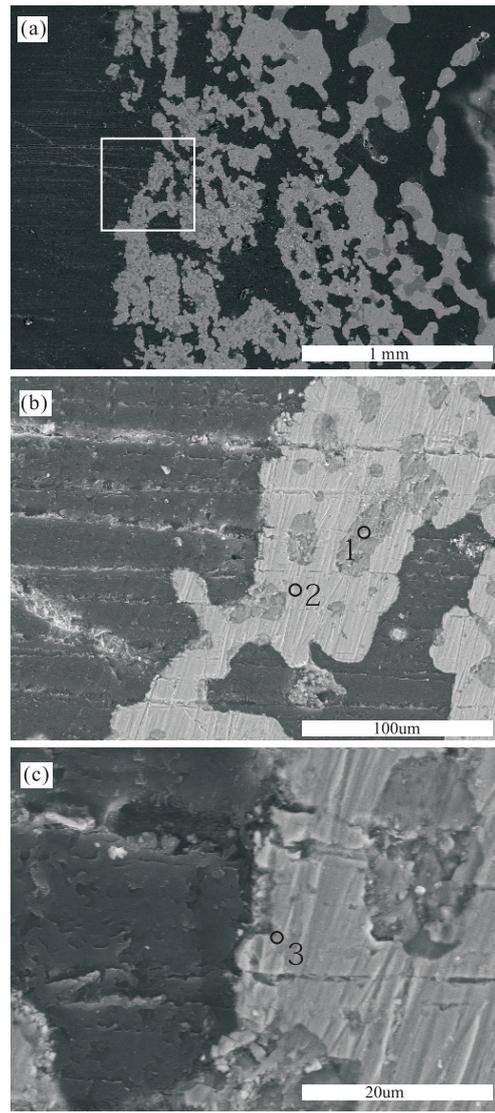


Fig.5. The specific portion and whole sample shrinkage % averaged by every individual DRI with different amount of coal type.



(d)	No. # 1	No. # 2	No. # 3
Element	Atomic %		
C	5.88	4.70	2.90
O	20.75	2.05	1.93
Al	3.22	N.D.	N.D.
Si	12.69	0.34	0.16
Ca	2.53	0.20	0.1
Fe	54.93	92.92	94.91
Total	100	100	100
Suggestion	Slag	Iron	Iron

Fig.6. SEM images and EDX analysis of sample A on the top layer DRI. (a) Low magnification image taken by near the surface of DRI. (b) Middle magnification image enlarged from the marked area in (a). (c) Middle magnification image zoomed in on the edge of DRI surface. (d) EDX analysis at the points in (b) and (c).

3.3 Degree of reduction, metallization and iron productivity

3.3.1 Bulk sample analysis

The detailed data of DCR percentage, Metallization percentage, Iron Productivity, and residual Carbon and FeO are listed in Table 5, which were plotted in Figs.7 to 10. The trend of average DRI shrinkage percentage, calculated DCR percentage and chemical analyzed metallization percentage is very similar. As the addition of coal A in the green balls was increased, the DRI shrinkage percentage, DCR percentage and metallization percentage were enhanced. The total metallization percentage of sample A, nearly reached 94%. However, the trend of iron productivity was opposite to

the other properties, shown in Fig.8. The factors that affected iron productivity was not only the metallization percentage but also the amount of iron metal reduced from iron oxide. In fact, the total weight of the green balls in sample C was higher than that of other green balls in the same loading volume, given in Table 4. The reason is that the green balls made of anthracite coal had more iron oxide content, causing a higher bulk density.

3.3.2 DRI layer analysis

The DRI metallization percentage from the top portion to the bottom portion in sample A trends up. On the contrary, the DRI metallization percentage in sample C trends down. It is suggested that the amount

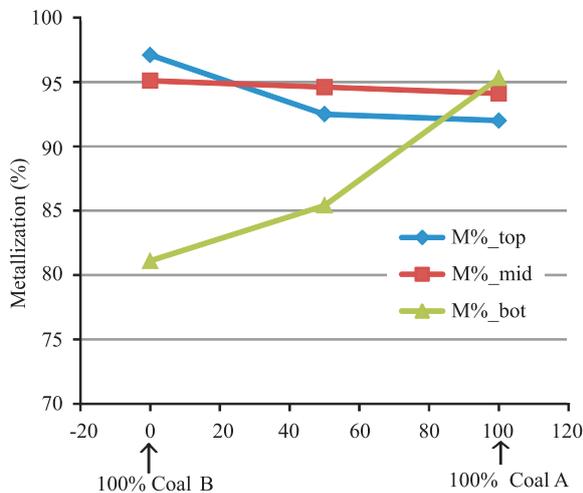


Fig.7. The specific portion metallization % with different amount of coal type.

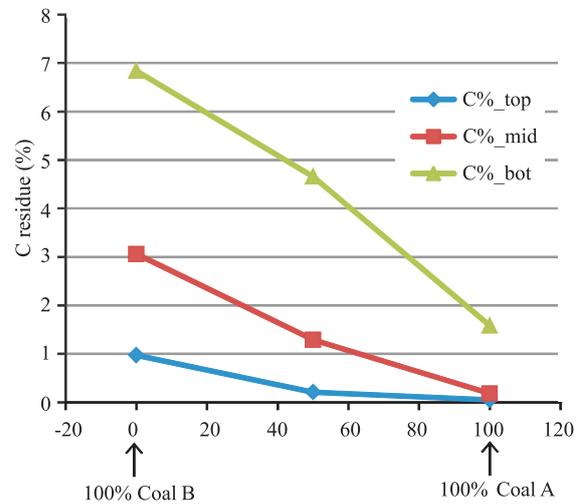


Fig.9. The carbon residue % plots in specific portion with different amount of coal type.

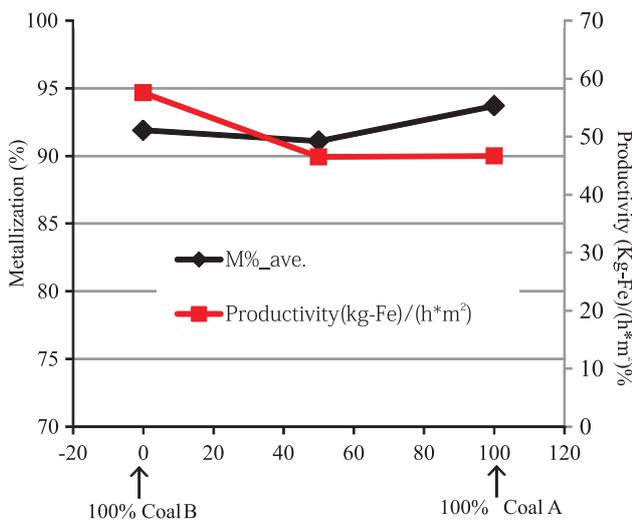


Fig.8. The whole sample metallization % and iron productivity with different amount of coal type.

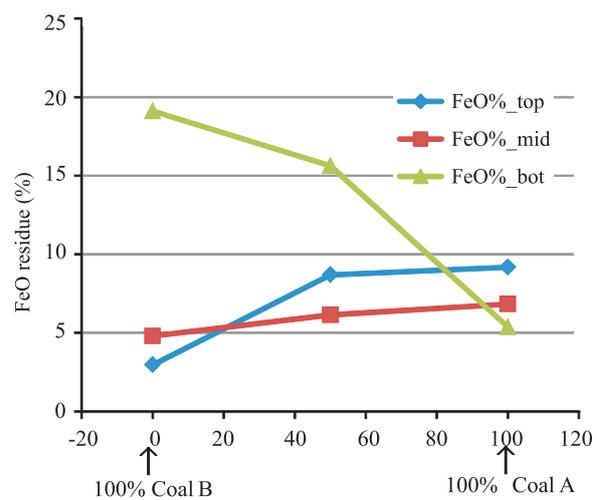


Fig.10. The FeO residue % plots in specific portion with different amount of coal type.

of VM in coal significantly affects the carbothermic reduction behavior of pellets in a tall bed.

Firstly, VM is a total combination of free carbon, oxygen and a small amount of hydrogen. Free carbon and a small amount of hydrogen in VM can also play the role of reductant to reduce the iron oxide and other reducible oxides in the pellets. However, usually VM is released before reaching the reducible temperature of iron oxide. Especially in the top portion of pellets, the released VM could easily escape from the pellet bed, causing the low carbon utilization. Consequently, because of the different amounts of VM in coal, the metallization percentage in the top portion of sample A was less than that of samples B and C although the calculated C/O ratio was the same at 1.1 in the green balls. The behavior of the released VM escaping the pellet bed is negative to the reduction reaction of the top portion of pellets. However, it is not so critical to the reduction reaction of the middle and bottom portion of pellets because the uprising released VM can also be utilized for the reduction reaction of top and middle portion pellets. Therefore, for sample A the metallization percentage of the bottom portion was relatively higher than that of the middle and top portions.

On the other hand, according to the report⁽⁷⁾, the reactivity of high VM coal is better than that of hard coal. Therefore, the reduction rate from top to bottom of sample A was higher than that of samples B and C, resulting in the metallization percentage in the bottom portion of sample A was higher than that of sample B and C. For sample B, the behavior of reduction and utilization of carbon were mainly caused in the middle so that the metallization percentage of the middle portion was relatively higher than that of the top and bottom portions.

3.3.3 Residual carbon and FeO analysis

Figure 9 is the carbon residue percentage plots of specific portions with different amounts of coal type. The carbon residue increased from top to bottom and also increased by increasing the addition of coal B. The carbon reductant was deficit on the top and middle portion of sample A at the C/O ratio of 1.1 because there were still about 5.0 to 7.0 % of FeO left to be reduced given the data in Fig.10. On the other hand, at the same C/O ratio of 1.1 in sample C, the carbon reductant was more likely surplus because there was still 1% of residue carbon left in the 97.1% metallization of the top DRI. The results repeatedly coincided with the fact that the carbon utilization of high VM coal A is less than that of anthracite coal B.

Combining the data of metallization percentage, residual carbon and FeO, the operation parameters are suggested as follows.

(1) Using the high VM coal as a reductant such as coal

A, it was supposed to obtain the higher metallization percentage and better quality DRI because the metallization percentage from top to bottom concentrate at a narrower range of 92 to 95%. However, the carbon utilization is relatively low especially in the top portion of pellets. It is suggested that slightly increasing the C/O ratio to 1.15 may be helpful to enhance the metallization percentage of the top portion DRI. On the other hand, shortening the reduction time is supposed to be beneficial to increasing the iron productivity.

(2) As for using anthracite coal as a reductant such as coal B, we can obtain higher iron productivity. As well as, the carbon utilization is relatively high. Therefore, we can save the carbon consumption by decreasing the C/O ratio in the green balls. However, the metallization percentage in the bottom portion is relatively low. Slightly extending the reduction time is suggested to increase the metallization percentage.

4. CONCLUSIONS

The experiments of carbothermic reduction in a tall pellet bed were carried out to study the effects of VM content of coal properties in ore/coal composite pellets. The temperature variations at the bottom of the pellet bed during whole reduction period were recorded; the DRI appearance, microstructure and chemical composition were investigated in bulk sample and a specific portion of the sample, respectively. The following conclusions can be drawn:

- (1) The ranking for the temperature increase at the bottom of the pellet bed with green balls with 33% VM coal, with a mixture of 33% plus 5% VM coal and with 5% VM coal. It is suggested that the pellets composed of higher amounts of VM in coal promotes the degree of DRI shrinkage percentage, causing the higher heat transfer rate from the top of the bed to the bottom of the bed.
- (2) Although the DRI appearances of the top layer were different because of the coal type, it is not a critical issue that affects the metallization percentage of DRI. The SEM/EDX analysis of the top layer DRI indicated that there was only a small amount of oxygen on the edge of the DRI surface, suggesting virtually no re-oxidation occurred on the DRI surface.
- (3) As for using high VM coal as a reductant such as coal A, it is supposed to obtain a higher metallization percentage and better quality DRI because the metallization percentage from the top of the bed to the bottom of the bed concentrate at a narrower range of 92 to 95%. However, the carbon utilization is relatively low especially in the top portion of the pellets.

- (4) As using anthracite coal as a reductant such as coal B, we can obtain higher iron productivity. As well as, the carbon utilization is relatively high. Therefore, we can save the carbon consumption by decreasing the C/O ratio in the green balls.

REFERENCES

1. Joseph Vehc and Wei-Kao Lu, Metec. In Steel Conf., Direct reduction: production and use of DRI, Session 10, 1, 2001.
2. Sabuj Halder, Doctoral Thesis, Carnegie Mellon University, Pittsburgh, PA, 2007 Wei-Kao Lu and Dianbing Huang, United States Patent, US 6257879 B1.
3. Wei-Kao Lu and Dianbing Huang, United States Patent, US 6592648 B2.
4. Wei-Kao Lu, AISI/DOE Technology Roadmap Program, under Cooperative Agreement, No. DE-FC07-97ID13554, Pittsburgh, PA, 2002.
5. Aswin Tejasukmana, P. Chris Pistorius and R. J. Fruehan, CISR progress report, June 2012.
6. Aswin Tejasukmana and P. Chris Pistorius, CISR progress report, May 2011. □