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COMPREHENSIVE REACTION BEHAVIOR OF A COKE MIXED BED UNDER BLAST FURNACE SIMULATED CONDITIONS WITH A CONSTANT LOAD[1]

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Abstract

Nowadays, further efficiency and flexibility for blast furnace ironmaking process are required to save ferrous and fuel resources, utilize low quality materials and lower reducing agent rates together with conserving global environment. In this work, as one of these measures, comprehensive reaction behaviors of the packed bed consisting of both pellet (alternative to sinter) and metallurgical coke particles were examined in a laboratory reaction apparatus with flowing a reducing gas N_2-CO-CO_2 under the blast furnace simulated conditions with a constant load until 1400°C, because these detailed reaction mechanisms are yet unknown. As a result, the mixing of coke in the bed enhanced to a definite extent the reducibility of pellets than those without coke, whereas the gasification of coke did not almost occur. Simultaneously the mixing of coke inhibited fairly the bed shrinkage derived from softening of packed materials and it was confirmed the role of coke in the bed as a hard spacer. Also, with increasing the proportion of coke mixed in the bed until 5 wt% and 10 wt%, the starting temperature of metal melting lowered surely due to enhancement of carburization into reduced irons derived from carbonous species in both phases of gas and coke. Moreover, the reaction behaviors of the bed were overall investigated along with the results of pressure drop and exit gas analysis and micro structures of partial reacted solids in the bed, including the influence of the size of coke.

Key words: Coke mixed packed bed; Reducibility; Carburization; Softening melting; Blast furnace simulated reaction behavior.

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1 INTRODUCTION

Nowadays the blast furnace is required to be operated under lower reducing agent rates against CO_2 exhaust reduction and raw materials resources issues. However, these operations necessitate higher ore/coke burden ratio and lead to difficulty such as deterioration of permeability due to reduction retardation and cohesive zone expansion. [1] As one of measures against these difficulty, nut coke mixing into ore layer was previously tried and it is known that it could accomplish enhancement of ore reduction and lowering of permeability resistance through cohesive zone etc..[2,3] Also, recently high reactivity coke and lowering of gasification start temperatures or thermal reserve zone temperatures have been further investigated[4-7] and it is expected that nut coke mixing would be effective to realize enhancement of gasification, regeneration of reducing gas, enhancement of indirect reduction, improvement of permeability and so on. [8] However, these detailed reaction mechanisms still remain unknown.

Therefore, this work aimed to carry out reaction tests of the packed bed consisting of both pellet (alternative to sinter) and metallurgical coke particles in a laboratory reaction apparatus under the blast furnace simulated conditions with a constant load in order to elucidate those comprehensive reaction behaviors fundamentally.

2 EXPERIMENTALS

2.1 Samples

As samples employed in reaction tests, we used mixtures consisting of iron ore mini fired pellet (1.7-2.8mm dia., chemical composition: Table 1, basicity of gangues:1.01) and metallurgical coke particles (0.85-1.7mm dia., chemical composition and property: Table 2). The contents of coke mixed in samples on the basis of pellet were given four conditions of 0, 5, 10, and 100% (wt%) and another condition of 5% (wt%) coke (0.425-0.85mm dia.) in order to investigate influence of smaller coke size on reaction behavior. (Hereafter, samples were named Pellet, 5wt%coke, 10wt%coke, Coke and 5wt% coke(s)) The height of samples in a packed bed was set to be constant 32mm, where pellet and coke in samples weigh as shown in Table 3. The apparent densities of pellet and coke particles were 3.06 and 1.08 g/cm^3 respectively.

2.2 High Temperature Reaction Test Under Load

Experimental reaction apparatus is shown in Fig.1.[6] A graphite supporting tube and a crucible (inner dia.: 18mm, height: 75mm, drilled 7 gas holes in the bottom) are coated with alumina water slurry and then dried to prevent reactions from reaction gas and sample. A sample is filled in the graphite crucible after layering small alumina balls (4mm dia.) in the lower part to adjust a bed height of 32mm. After putting the graphite plug with gas holes on the upper of sample and then applying 1kg load on it, reaction test is performed from room temperature to 1400^{o}C under the heat pattern and gas contents (N_2-CO-CO_2 mixture) simulated on the basis of real blast furnace as shown in Fig.2 (thermal reserve zone temperature: 1000^{o}C, gas flow rate: 1Nl/min).

Shrinkage of sample, gas pressure drop through the packed bed and exit gas analysis by means of infrared radiation absorption are measured automatically during the reaction. Reaction tests were performed until predetermined times (82.5min (750^{o}C), 110min (1000^{o}C), 140min (1000^{o}C), 160min (1100^{o}C), 180min (1200^{o}C), 200min (1300^{o}C), 220min (1400^{o}C)) and then the samples were rapidly cooled down to room temperature in N_2 stream to protect them from their oxidization. For these partial reacted samples, weight loss, determination of carbon and sulfur contents and observation in cross section by optical microscope and so on were performed.

Table 1 Chemical composition of mini pellet (mass%) .

T.Fe	ΣO	Al_2O_3	SiO_2	CaO	MgO	S	P
66.23	28.46	0.75	1.56	1.57	0.85	0.007	0.047

Table 2 Proximate analysis (mass%) and properties of coke.

Ash	VM	T.S.	T.C.	DI	CRI	CSR
11.85	0.86	0.61	86.98	86.3	28.5	62.5

Table 3 Sample weight (mass%) .

Sample	Total weight (g)	Coke (g)
Pellet	14.60	0.00
Pellet+5wt%coke	13.44	0.67
Pellet+10wt%coke	12.50	1.25
Pellet+5wt%coke(s)	13.44	0.67
100wt%coke	4.80	4.80
100wt%coke(s)	5.20	5.20

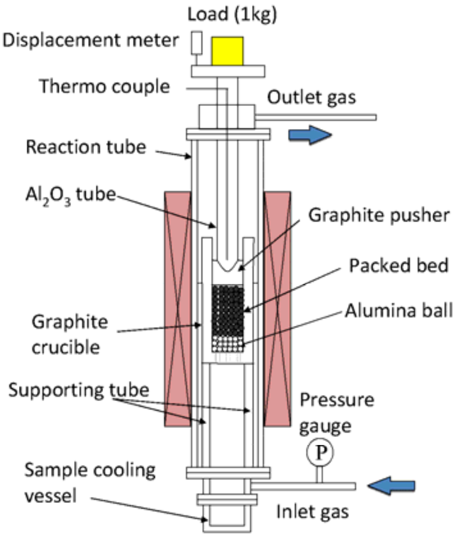

Fig.1 Blast furnace simulated reactor.

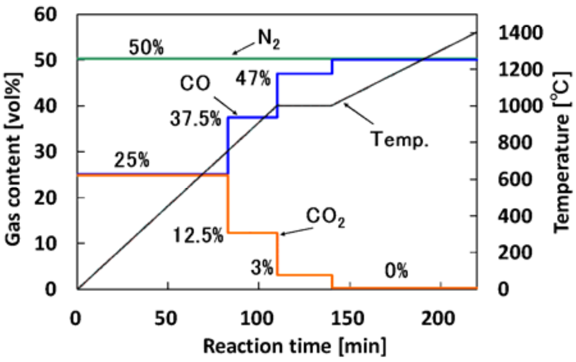

Fig.2 Experimental conditions (Flow gas and heat pattern).

3 RESULTS AND DISCUSSION

3.1 Weight Loss and Reduction Degree

Figure 3 shows variation of weight loss degrees with reaction time for Pellet and 5wt%coke samples, where broken lines indicate theoretical weight loss degrees corresponding to reducible oxygen. Around 1100-1400°C both of them almost reached theoretical ones. Until nearly 1100°C reduction of iron oxide in pellets seems to finalize. Also, Coke sample gave weight loss as small as 0.1% until 1400°C and did not almost react with gas because of low reactivity CRI=28.5 in Table 2. From this result, it is supposed that gasification of coke would not almost occur ($C(s)+CO_2(g)\rightarrow 2CO(g)$).

Figure 4 shows variation of reduction degrees with reaction time for Pellet and 5wt%coke samples, which were calculated from weight loss. Both samples indicated almost similar tendency, while small deference appeared to be 2% and 7% larger than Pellet sample for 5wt%coke and 10wt%coke samples at 1000°C (140min) respectively.

Around 1300-1400°C mixing coke provided a little larger reduction degrees than Pellet sample probably due to direct reduction of gangue species in pellets by coke or carbon in metallic iron.

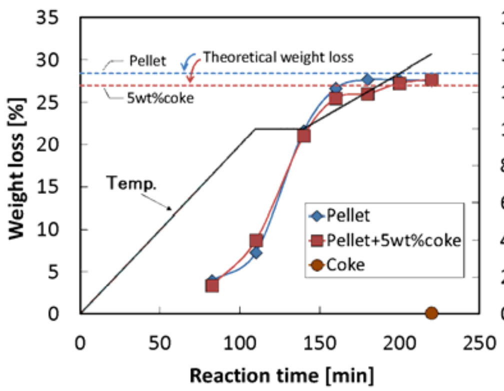

Fig.3 Weight loss with reaction time.

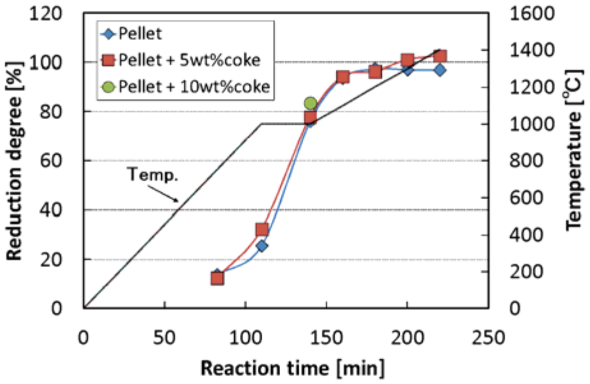

Fig.4 Reduction degree with reaction time.

Figure 5 shows variation of reduction degrees with mixing coke content for 1000°C (140min), showing higher reduction degrees with increasing mixing coke content and smaller coke size. Watakabe et al.[1] reported similar enhancement of reduction by coke mixing in the bed comprised mainly of sinter. Their results in 1200°C were also contained in the figure which were nearly corresponding to ours.

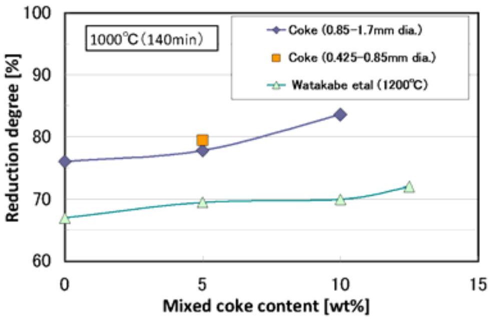

Fig.5 Reduction degree with mixed coke content.

Table 4 shows comparison of experimental conditions with those in Watakabe et al.[1] as other researches. The reason for this work to provide10-15% larger than their reduction degrees would be due to smaller ore particles and half ore/gas if both reducibilities of ferrous ore samples not taking into consideration.

Table 4 Comparison of experimental conditions with other researches.

	Mass of ore bed (g)	Bed dia. (cm)	Gas flow rate (Nl/min)	Ore particle dia. (cm)	Ore/Gas (g/Nl)
This work	14.6	1.8	1	0.17–0.28	14.6
Watakabe etal	900	10	30	1–1.5	30

3.2 Analysis of Exhaust Gas

Figure 6 shows their gas contents difference of exit gas from basic inlet CO and CO_2 with reaction time for three samples (a) Pellet only, (b) 5wt%coke and (c) Coke only which were measured by means of infrared radiation absorption. These variations would be caused by generation and consumption of both gas species derived from reduction and gasification reactions.

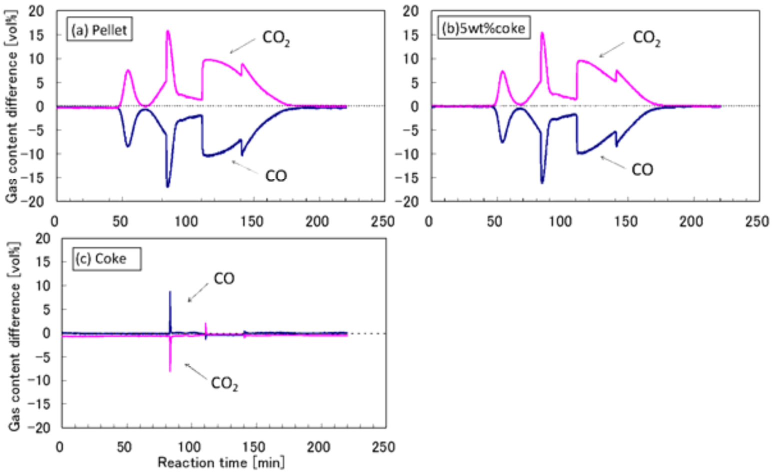

Fig. 6 Gas content difference of exit gas from basis, (a) Pellet only, (b) 5wt%coke, (c) Coke only.

When indirect reduction of iron oxides ($Fe_mO_n(s)+CO(g)\rightarrow Fe_mO_{n-1}(s)+CO_2(g)$) occur, their gas contents difference from basic inlet CO and CO_2 will be equal. When gasification of coke ($C(s)+CO_2(g)\rightarrow 2CO(g)$) occur, their gas contents difference from basic inlet gases will appear as duplicate values. Also, though gas carburization ($2CO(g)\rightarrow C(\text{in Fe})+CO_2(g)$) may occur in high temperatures, these reactions will be negligible due to a few % carbon in iron.

From Fig.6, both gas species contents changed around 50min (450^oC) except Coke sample. This would be due to reduction of Fe_2O_3 to Fe_3O_4. After that both gas contents difference also changed around 70min (640^oC). This would be due to reduction of Fe_3O_4 to FeO. Then, with heating and changing both gas contents difference (sharp change around 82.5min, 110min and 140min due to switching inlet gas contents (Fig.2)) metallization of FeO would mostly proceed.

For all samples, their gas contents difference from basic inlet gases disappeared beyond 180min (1200^oC), supposing that reduction of iron oxides in pellets would be finalized. Also, their gas contents difference from gasification of coke were not recognized for both 5wt%coke and Coke samples, showing gasification of coke did not almost occur during all tests.

In previous researches [2] it was reported that enhancement of reduction by mixing coke into ore layer is caused by reduction of iron oxides with CO gas generated by gasification of coke. In this work it was supposed that mutual effects by both reactions of reduction and gasification were not recognized because reduction of iron oxides mostly finalized before gasification of coke occurred actively in high temperatures. Therefore, enhancement of reduction around 140min (1000^{o}C) as shown in Figs.4 and 5 would be caused by improvement of gas permeability in the bed by the existence of coke spacer. (Section 3.3)

Figure 7 shows time dependence of reduction degrees calculated from the results in Fig.6 and total exit gas flow rates together with those from weight loss for both 5wt%coke and Coke samples, showing both results seemed approximately accordance for both samples.

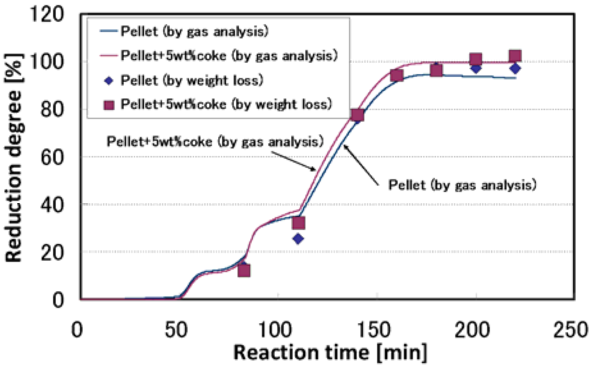

Fig.7 Reduction degree with reaction time. (by weight loss and gas analysis)

3.3 Packed Bed Structures after Reaction

Figure 8 shows cross section of packed beds after partial reaction and the schematics for both Pellet and 5wt%coke samples. For both samples the beds shrank and the spaces in the beds decreased with reaction time and temperatures. However, 5wt%coke samples seemed to possess larger spaces in the beds relatively to Pellet samples. This would be likely due to suppression of sintering among individual pellets and enhancement of gas permeability and indirect reduction under coke mixing.[9] Moreover, for 5wt%coke samples the melting of pellets took place in 1400^{o}C. This would be because carburization to metallic iron (solid carburization from coke or gas carburization by CO gas, Fig.17) for the sample proceed to be lowered the melting start temperature.

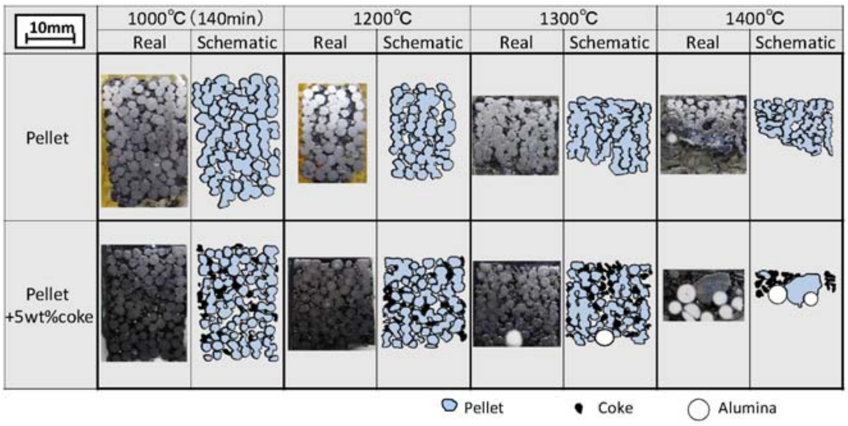

Fig.8 Cross section of packed beds after partial reaction and the schematic.

3.4 Packed Bed Shrinkage and Pressure Drop

Figures 9 and 10 show shrinkage degrees in the beds with reaction time for each sample. From Fig.9 it is seen the beds expanded a little around 50min (450°C)-78min (700°C) except Coke sample, probably because of crystalline transformation during reduction of Fe_2O_3 to Fe_3O_4. Then, because metallic iron appeared beyond nearly 1000°C, the shrinkage degrees seemed to become larger together with shrinkage by sintering and softening of metallic irons with increasing temperatures.

On the other hand, Coke sample did not almost shrink during reaction. For 5wt%coke and10wt%coke samples the shrinkages were suppressed relatively to Pellet sample around 1000-1350°C. These would be because coke in these samples did not shrink similarly to Coke sample and had a role of hard spacer in the beds. Moreover, as mentioned in Sec. 3.3, it would be also caused by suppression of sintering among individual pellets under coke mixing.

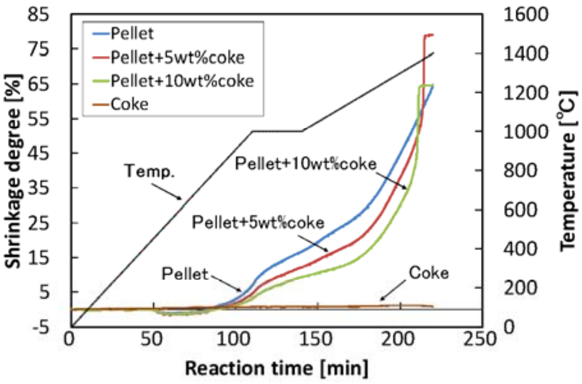

Fig.9 Shrinkage degree with reaction time.

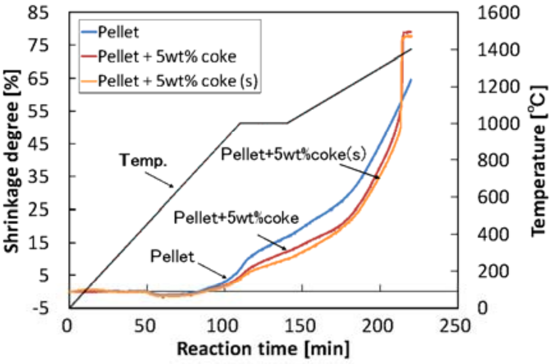

Fig.10 Shrinkage degree with reaction time (Comparison of coke size).

For 5wt%coke and 10wt%coke samples, rapid increase of shrinkage degrees probably by melting of pellets was observed beyond 1300°C, the temperatures of which occurred are shown in Table 5(a), being given 1366°C for 5wt%coke and 1349°C for 10wt%coke samples. The temperature for the latter was lower than the former. This would be because the latter had (1) more solid carburization with larger contacts among coke and pellet particles and (2) more gas carburization with improvement of gas permeability in the bed with increasing coke.

Table 5 Time and temperature at shrinkage rapidly increasing (a), pressure drop rapidly increasing (b), and maximum pressure drop (c).

(a)	Time (min)	Temp.(℃)
Pellet	-	-
+ 5wt%coke	213.3	1366
+ 10wt%coke	208.8	1349
+ 5wt%coke(s)	212.7	1363

(b)	Time (min)	Temp.(℃)
Pellet	-	-
+ 5wt%coke	214.3	1370
+ 10wt%coke	206.5	1330
+ 5wt%coke(s)	213.7	1368

(c)	Maximum pressure drop (kPa)	Time (min)	Temp.(℃)
Pellet	0.90	101.1	916
+ 5wt%coke	2.67	214.6	1372
+ 10wt%coke	1.70	220.0	1400
+ 5wt%coke(s)	5.16	214.0	1369

Figure 10 show shrinkage degrees in the bed with reaction time for 5wt%coke(s) sample. From this figure it is seen that smaller coke size suppressed a little shrinkage in the bed with reaction time and the temperature for rapid increase of shrinkage degree also shifted a little lower. (Table 5(a)) These would be because they were caused by (1) more solid carburization with larger contacts among coke and pellet particles and partly (2) more gas carburization probably with improvement of gas permeability in the bed, as mentioned above.

Figure 11 shows variation of shrinkage degrees in the bed with mixing coke contents for each temperature, being confirmed higher shrinkage degrees with increasing temperatures and lower shrinkage degrees with mixing coke contents. It was reported by Watakabe et al.[1] that shrinkage in the beds consisting mainly of sinter was suppressed with mixing coke. In the figure, their results were added for 1300°C and compared with this work. Though their results indicated higher shrinkage than this work as a whole, both results seemed to have a similar tendency.

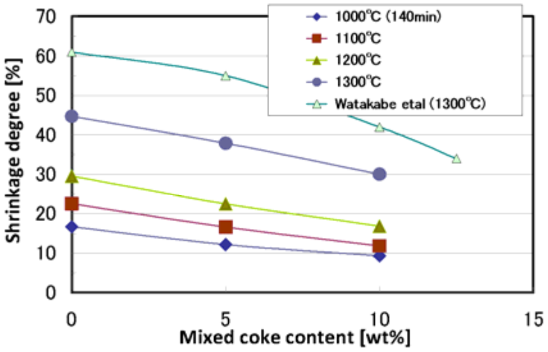

Fig.11 Shrinkage degree with mixed coke content.

Figure 12 shows variation of gas pressure drop through the bed with reaction time for each sample. Though Pellet sample was not observed rapid increase of pressure drop during reaction, coke mixing samples were observed the rapid increase. Then, the time and temperature at which rapid increase of pressure drop and maximum pressure drop occurred were summarized as shown in Tables 5(b) and 5(c) respectively. The rapid increase of pressure drop took place at lower temperatures in order of 10wt%coke, 5wt%coke(s) and 5wt%coke samples. These were also corresponding to the order of lower temperatures for rapid increase of shrinkage degrees as mentioned above. The rapid increase of pressure drop would be caused probably by partial melting of metallic iron (melting start) with increasing temperatures and progress of carburization.

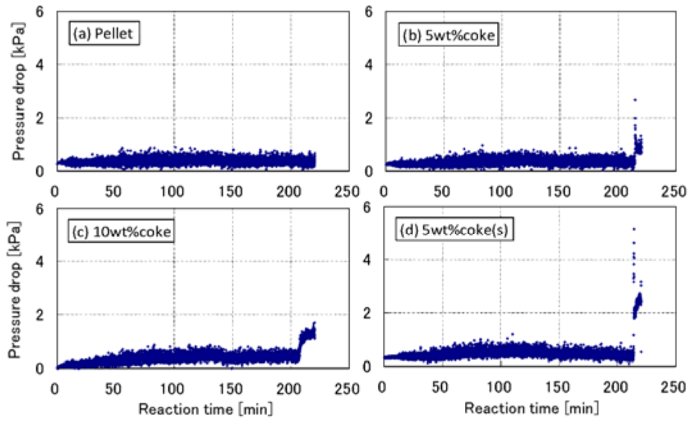

Fig.12 Pressure drop through packed beds with reaction time.

Moreover, maximum pressure drop occurred as the highest for 5wt%coke(s) sample. Because 10wt%coke sample has a larger volume of coke in the bed relatively to other samples and retain higher gas permeability than others, their maximum pressure drop would become lower relatively.

3.5 Micro Structures of Packed Bed after Reaction

Figures 13(a) and (b) show micro structures of cross section in the core of pellets in the center part of the beds after partial reaction (1300^{o}C) for Pellet and 5wt%coke samples respectively, showing that 5wt%coke sample has smaller iron particles and less sintering among them than Pellet sample. This would be because the former had easier gas permeability in the bed by mixing coke and earlier progress of reduction relatively to the latter and was suppressed both sintering among iron particles and softening of the bed derived from FeO bearing melting slag. Further it is supposed that the former would be facilitated gas carburization to metallic iron due to easier gas diffusion into the internal portion in pellets.

Figures 14(a) and (b) show micro structures of cross section in the central and the lower parts of the bed after reaction (1400^{o}C) for Pellet sample, respectively. For Fig.14(b) it is seen that liquid slag containing gangue species was exuded from the pellets in the lower of the bed, supposing that unreduced FeO in the core of pellets assimilated with gangue species and the low melting slag was formed to be exuded in the surface via metallic shell of pellets,[10,11] while pellets in the central of the bed as shown in Fig.14(a) were not observed the exudate as seen in Fig.14(b).

Figures 15(a) and (b) show micro structures of cross section in the outer and the center of metallic melt left in the beds after reaction (1400^{o}C) for 5wt%coke sample respectively. In the outer part, kish graphite was confirmed, whereas it was not in the central part, supposing that carbon contents were different between their parts. It is supposed that the outer part reached pereutectic composition and the center part reached hypoeutectic composition showing micro structures coprecipitated γ-Fe and graphite from melt remained after initial γ-Fe precipitates.

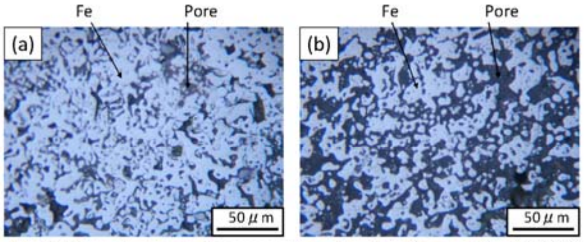

Fig.13 Microstructures of cross section of pellet after reaction (1300°C), (a) Pellet only, (b) 5wt%coke.

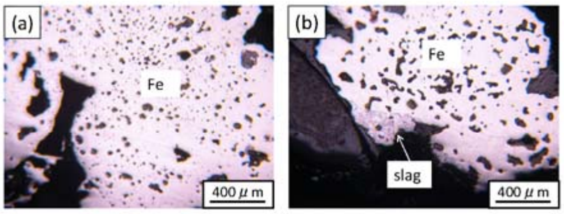

Fig.14 Microstructures of cross section of pellet after reaction (Pellet,1400°C), (a) central part, (b) lower part.

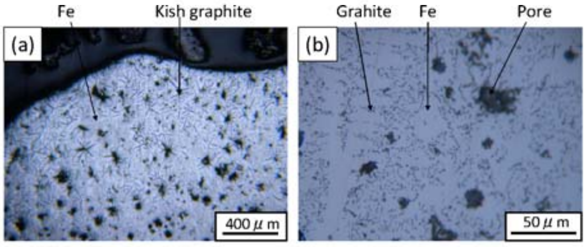

Fig.15 Microstructures in cross section of metallic melt after reaction (5wt%coke,1400°C), (a) outer, (b) center.

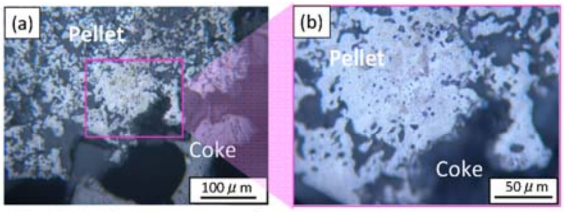

Fig.16 Etched microstructures of cross section of pellet contacted with coke after reaction (5wt%coke, 1300°C).

Figures 16 show micro structures etched cross section of parts contacted between coke and metallic iron particles in the bed after reaction (1300°C) for 5wt%coke sample in order to further investigate the carburization behavior, where (b) photo was magnified (a) photo. In the area in which metallic iron was formed, much pearlite was formed, showing the carburization was enhanced in the parts to suggest solid carburization to metallic iron could proceed actively beyond 1300°C.

3.6 Carbon Content in Iron

The partial reacted samples were first crushed and then separated to metallic iron part under ultrasonic and magnetic power inside ethanol liquid to be supplied to chemical determination analysis by a combustion method with oxygen. The obtained carbon contents in metallic iron are shown within Fe-C binary equilibrium diagram in Figure 17, where dotted lines indicate stable Fe-graphite system.

For Pellet samples, CO gas carburization appeared surely beyond 1000°C when metallic irons begin to be formed and the carbon contents increased with raising temperatures to reach 0.87% close to the solidus curve at 1400°C.

For Coke mixing samples the contents increased more beyond 1100°C in comparison with Pellet samples. This would be because (1) solid carburization by coke and (2) enhancement of gas carburization with easier permeability by coke mixing. At 1400°C the carbon contents increased rapidly to reach nearly 4% close to the eutectic composition.

Moreover, the carbon contents in 1300°C became larger in order of 10wt%coke, 5wt%coke(s) and 5wt%coke samples. These were also corresponding to the order of lower temperatures for rapid increase of pressure drop (melting start) by coke mixing as mentioned in Sec.3.4.

As a summary, Figure 18 shows carbon content in metallic iron and melting start temperature with mixing coke contents for 1300°C, supposing the effect of carbon content before melting on melting start temperatures.

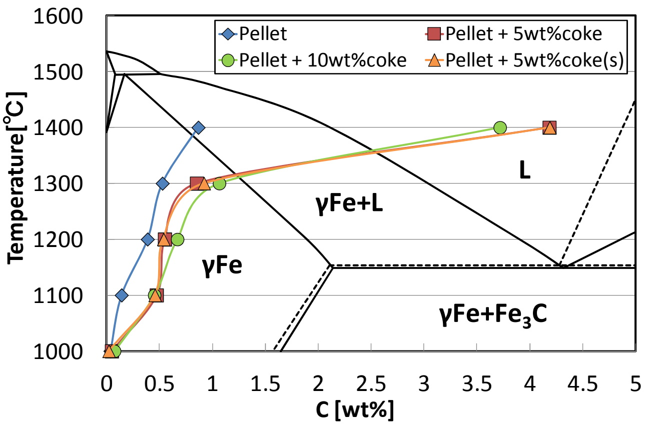

Fig.17 Carbon content in metallic iron inside Fe-C phase diagram.

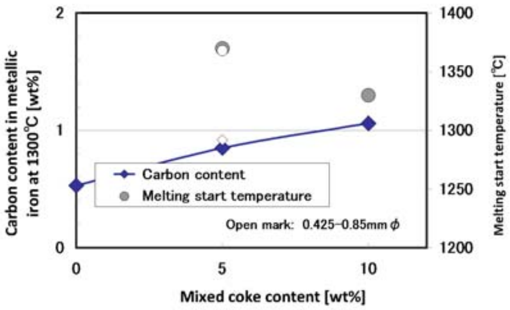

Fig.18 Carbon content in metallic iron at 1300°C and melting start temperature with mixed coke content.

3.7 Overall Discussion

Because coke employed in this work has a low reactivity of CRI=28.5, synergy effects from mutual reactions between reduction and gasification based on adjacent arrangements of pellet and coke particles were not almost recognized inside the packed bed consisting of both particles, exclusive of reaction behaviors concerning both enhancement of permeability through the bed and direct carburization. In order to further enlarge these synergy effects, coke size control[8] and utilization of high reactivity coke or ferro coke[4,7,12,13] would be also required including the investigation to improve the reactivity of coke taking account of physical properties of coke (DI, CRS). It is also expected that researches to investigate both reducibility and property of ferrous burdens[13,14] would be carried out anyhow.

Moreover, regarding softening shrinkage[10,11] and carburization melting behaviors in the range of high temperatures, optimization of the packed bed structures consisting of reductants and ferrous burdens, thinning of cohesive zone[15] and so on should be further investigated from the comprehensive viewpoints to improve the blast furnace process efficiency bravely.

4 CONCLUSIONS

Reaction tests of the packed bed consisting of both pellet (alternative to sinter) and metallurgical coke particles were carried out in a laboratory reaction apparatus with flowing a reducing gas N_2-CO-CO_2 under the blast furnace simulated conditions with a constant load in order to elucidate those comprehensive reaction behaviors fundamentally. The followings were included.

(1) The coke mixing enhanced surely reduction of pellets around 140min (1000°C). This would be caused by improvement of gas permeability in the bed by the existence of coke spacer, because gasification of coke did not almost occur.

(2) The shrinkage of the bed was suppressed with increasing coke mixing. This would be because gas permeability in the bed was facilitated by mixing coke, progress of reduction was enhanced and sintering of metallic iron derived from FeO bearing melting slag was suppressed to lower the shrinkage with softening of the bed, including a role of coke as a hard spacer in the bed.

(3) Coke mixing samples provided the rapid increases of pressure drop in the beds during heating around 1300-1400°C. These rapid increases derived from melting start by carburization to metallic iron took place at lower temperatures in order of 10wt%coke, 5wt%coke(s) and 5wt%coke samples. These were also corresponding to the order of lower temperatures for rapid increase of shrinkage degrees and carbon contents in metallic iron at 1300°C.

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