Carburization and Melting of Hot Compacted Iron in a Coke Bed

J. Park[1], M. Kim[2], I-K. Suh[3], and E. Kim[4], and J. Lee[5]

1.Researcher, POSCO, Gwangyang 57807 South Korea. Email: J_park@posco.com
2.Research Engineer, Hyundai Steel, Dangjin 31719 South Korea. Email: mkkim26@hyundai-steel.com
3.Industry-Co. Professor, Korea University, Seoul 02841 South Korea. Email: iksuh@korea.ac.kr
4.PhD Candidate, Korea University, Seoul 02841 South Korea. Email: kukuridie@korea.ac.kr
5.Professor, Korea University, Seoul 02841 South Korea. Email: joonholee@korea.ac.kr

Keywords: carburization, hydrogen-enriched ironmaking process, iron ore sinter; melting; hot compacted iron

ABSTRACT

One of the key technologies in developing hydrogen-enriched ironmaking operations is the control of the carburization, melting, and dripping behavior of the iron ore burden materials. When a hot compacted iron (HCI) is charged in the blast furnace or the FINEX Melter-Gasifier, iron oxide reduction, the reduced iron's carburization, and the melting of iron and slag occur successively. This study investigated the reduction, carburization, melting and dripping behaviour of HCI under a CO-H_2 gas mixture using the high-temperature X-ray radiographic technique. Under 100% CO gas atmosphere, the dripping temperature was 1410°C. When 5% H_2 was introduced, the dripping temperature slightly decreased to 1400°C. Furthermore, the dripping temperature gradually increased as the H2 gas composition increased. As 30% H_2 was introduced, the dripping temperature reached 1414°C. The carbon concentration in the drained metal samples gradually increased with increasing H_2 composition. It is considered that H_2 decreased FeO content in the slag, yielding the increased melting temperature and viscosity of the slag. On the other hand, H_2 accelerated the carburization of the reduced iron by CO gas, enabling the homogenization of the oxide materials to form a liquid phase. Therefore, it is considered that introducing H_2 in the reactor is helpful to increase productivity and energy efficiency by accelerating the liquid phase's formation.

INTRODUCTION

Steel is recognized as an essential material for sustainable development [IEA 2020]. Steel is used as an essential core material in renewable energy production, such as solar and wind power generation and nuclear power generation. Steel is also used as the core material of energy-efficient transportation: automobiles, ships, and trains. For example, steel is used for electric vehicle bodies, battery packs, and electric motors. The adoption of steel is also increasing for zero-energy building construction. At the same time, however, the demand for the reduction of greenhouse gas emissions from the iron- and steel-making processes cannot be ignored; the steel industry emits about 7% of global greenhouse gas emissions [IEA 2020], so the development of new zero-carbon processes is required.

Technology that utilizes hydrogen in the blast furnace process and FINEX process is considered the most realistic alternative to reduce greenhouse gas emissions [Yi 2019]. New iron ore burdens have been developed to be used in the H_2-enriched ironmaking process [Park 2023b], [Park 2022], [Park 2020], [Rajavaram 2016]. Here, low-reduced iron (LRI) is charged in the blast furnace or in the Melter-Gasifier as a form of hot compacted iron (HCI) [Yi 2021]. As the hydrogen is introduced in the reactor, the reduction of iron oxide is accelerated, and the liquid slag formation temperature increases [Lan 2020], [Long 2016]. Accordingly, the melting and dripping temperature of burden materials would be delayed, when compared to the conventional blast furnace operation [Dereje 2018]. Then, a stable gas permeability in the coke bed becomes complex to establish, and the efficient heat transfer from the gas to the burden materials would not be guaranteed. Consequently, controlling the holdup of liquid phases in the coke bed will be difficult.

In the coke bed, the carburization of the reduced iron generally takes place in advance, yielding successive liquid slag formation by homogenizing the oxide phases [Park 2021]. Therefore, much attention is paid to the acceleration of the carburization of the reduced iron. Fruehan reported that the carburization of solid iron was enhanced by introducing H_2 gas [Fruehan 1973]. Shin et al. carried out a series of experiments and revealed that the carburization was affected mainly by the ash content in the coke [Shin 2014], [Shin 2012] [Jang 2012b]. Shin et al. also reported that FeO content lowered the carburization and melting behavior of the reduced iron [Shin 2015]. Kim et al. suggested that the reaction was accelerated due to Marangoni flow [Kim 2001]. Despite much research on this matter, no report has been published for in-situ observation of the carburization, melting, and dripping behavior of the HCI sample under the CO-H_2 gas atmosphere.

Recently, the high-temperature X-ray radiographic technique has been utilized to investigate liquid phases' melting and dripping behavior through the coke bed [Shin 2010], [Park 2021]. In the present study, the carburization, melting, and dripping behavior of HCI in the coke bed is investigated by using the high-temperature X-ray radiographic method. Here, the effect of the composition of the CO-H_2 gas mixture is investigated.

EXPERIMENTAL

The experimental apparatus comprised a $MoSi_2$ resistance furnace and a high-temperature X-ray radiographic inspector system. A schematic illustration is shown in Fig. 1. An alumina reaction tube (inner diameter of 90 mm and length of 1000 mm) was placed vertically in the furnace. Coke particles of 8~9 mm diameter were charged in a graphite crucible (inner diameter of 55 mm and height of 75 mm) with 33 holes of 5 mm diameter drilled in the bottom. There were four layers of coke particles in the crucible. An ellipsoidal-type HCI sample (longer-axis length of 3.8~4.7 mm, shorter-axis length of 3.1~3.3 mm, and height of 1.5~2 mm) was then placed on the top of the coke layer. The samples used in this study were provided by POSCO. The chemical compositions of the HCI are given in Table 1. The reduction degree of HCI is 57.2%. The chemical composition of the coke and its ash contents are given in Tables 2 and 3, respectively. The sample assembly was covered by a graphite lid, and it was heated to 1000°C at a heating rate of +5°C/min under an N_2 gas atmosphere. From 1000°C, the reaction gas was changed into a CO or CO-H_2 gas mixture with a predetermined mixing ratio. The reaction gas was blown on the surface of the HCI sample with a flow rate of 1 L/min STP through an alumina lance (inner diameter of 6 mm) with a distance of 10 mm. The melting and dripping behavior of metal and slag was investigated with the high-temperature X-ray radiographic system with a tungsten target X-ray tube. The experiment finished at 1500oC, and the sample was cooled to room temperature in the furnace. After experiments, the carbon and sulfur compositions of the drained metal samples were analyzed with LECO-C/S analyzer.

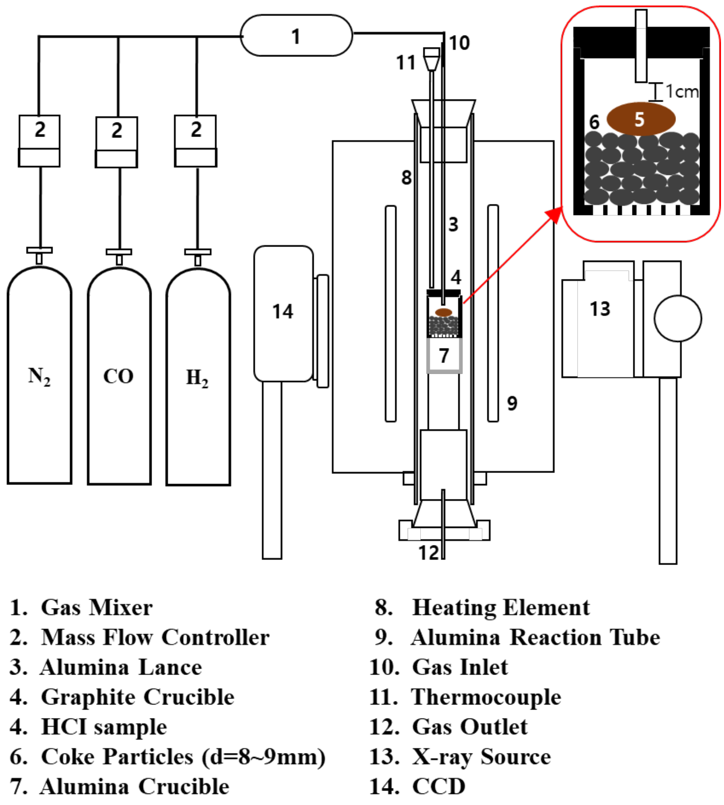

FIG 1 – Experimental apparatus for in-situ observation of carburization and melting

TABLE 1 – Chemical composition of the HCI sample

Element	Total Fe	Metallic Fe	FeO	CaO	SiO_2	Al_2O_3	MgO
wt%	72.2	32	36	3.7	4.2	2.1	1.2

TABLE 2 – Chemical composition of the coke particle

Element	Fixed C	Ash	Volatile Matter	Moisture
wt%	86.36	11.66	1.76	0.22

TABLE 3 – Chemical composition of the ash contents in the coke

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	P_2O_5	MgO
wt%	54.55	27.40	6.08	2.78	1.28	1.09	0.87

RESULTS AND DISCUSSION

Ex-situ Observation

Fig 2 shows the top view and the cross-section view of the sample assembly. It is considered that the amount of metal holdup decreased while the slag holdup increased. The color of the slag was changed from grey-green to white, indicating that the FeO content in the slag gradually decreased. Fig. 3 shows the carbon and sulfur contents of the drained metal samples. The carbon concentration gradually increased, whereas the sulfur concentration monotonically decreased. Since the contact between the reduced iron and the coke particles was not controlled precisely, it is more reasonable to investigate the general trend of the chemical composition change with increasing the H_2 concentration in the gas mixture. Here, the decrease in the sulfur content supported the idea that the carburization reaction by the CO-H2 gas mixture was more pronounced than that by direct contact with coke particles because the sulfur source was the coke [Lee 2007]. Accordingly, it is speculated that the increased H_2 concentration accelerated the reduction of iron oxide, which might increase the melting point of the slag, while increasing the slag viscosity [Nakamoto 2004].

Consequently, the slag holdup increased with increasing H_2 concentration. This observation shows a similar trend as the experimental results of Shin et al. [Shin 2015] with designed model experiments. In this study, the ash content would prevent carburization by solid coke [Jeong 2012b]. Park et al. reported that solid ash or high-viscosity liquid ash slag might prevent the carburization reaction by direct contact with coke particles [Park 2023a]. Therefore, there were more chances for the CO-H_2 gas mixture to provide the carbon source for the reduced iron.

In-situ Observation

Fig 4 shows the in-situ observation results of the sample assembly under a CO gas atmosphere. At 1280°C, liquid slag first appeared. Liquid metal formation was first investigated from 1380°C. This carburization and melting might be accelerated by the involvement of the FeO-containing slag [Kim 2001]. The liquid metal suddenly started to drain at 1409°C, while liquid slag remained in the coke bed. The drain of liquid slag occurred when the liquid metal pulled the liquid slag together. The liquid slag flew over the surface of liquid metal. A similar observation was reported by Jeong et al. [Jeong 2013]. However, in the present experiment, some part of the liquid metal eventually remained in the coke bed.

Fig. 5 shows the in-situ observation results when the CO-20%H_2 gas mixture was introduced. In this experiment, the first liquid slag formation was investigated at 1280°C, which is the same as the experiment with 100% CO gas. The liquid metal formation appeared at 1403°C. Due to the rapid reduction of iron oxide by H_2 gas, the carburization would not be enhanced by the existence of liquid slag. At 1405°C, the drain of liquid slag was investigated, followed by the drain of liquid metal. It is considered that the introduction of H2 gas enhanced the carburization by CO gas.

FIG 2 – Top and cross-section views of the sample assembly after experiments. The gas composition was varied (a)100% CO, (b) 95%CO-5%H_2, (b) 80%CO-20%H_2, (c) 75%CO-25%H_2, and (d) 70%CO-30%H_2. The drained metal and slag samples are shown separately.

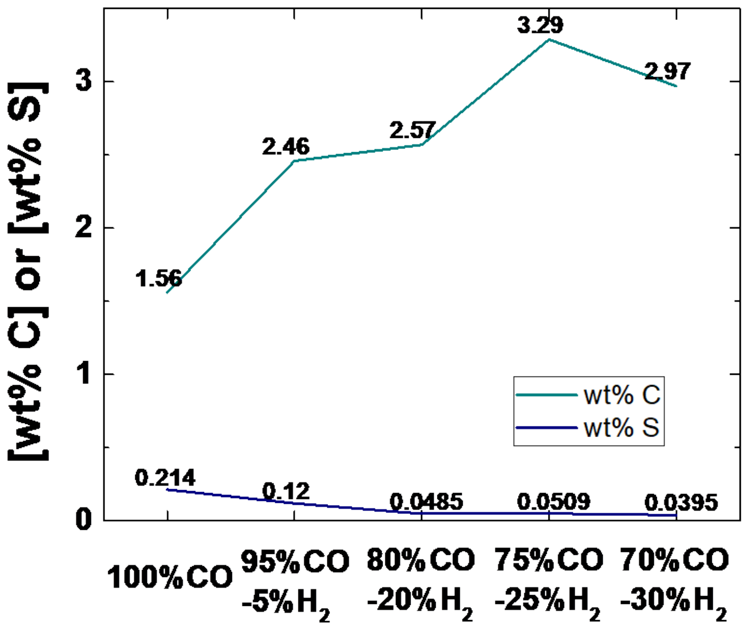

FIG 3 – Top and cross-section views of the sample assembly after experiments. The gas composition was varied (a)100% CO, (b) 95%CO-5%H_2, (b) 80%CO-20%H_2, (c) 75%CO-25%H_2, and (d) 70%CO-30%H_2. The drained metal and slag samples are shown separately.

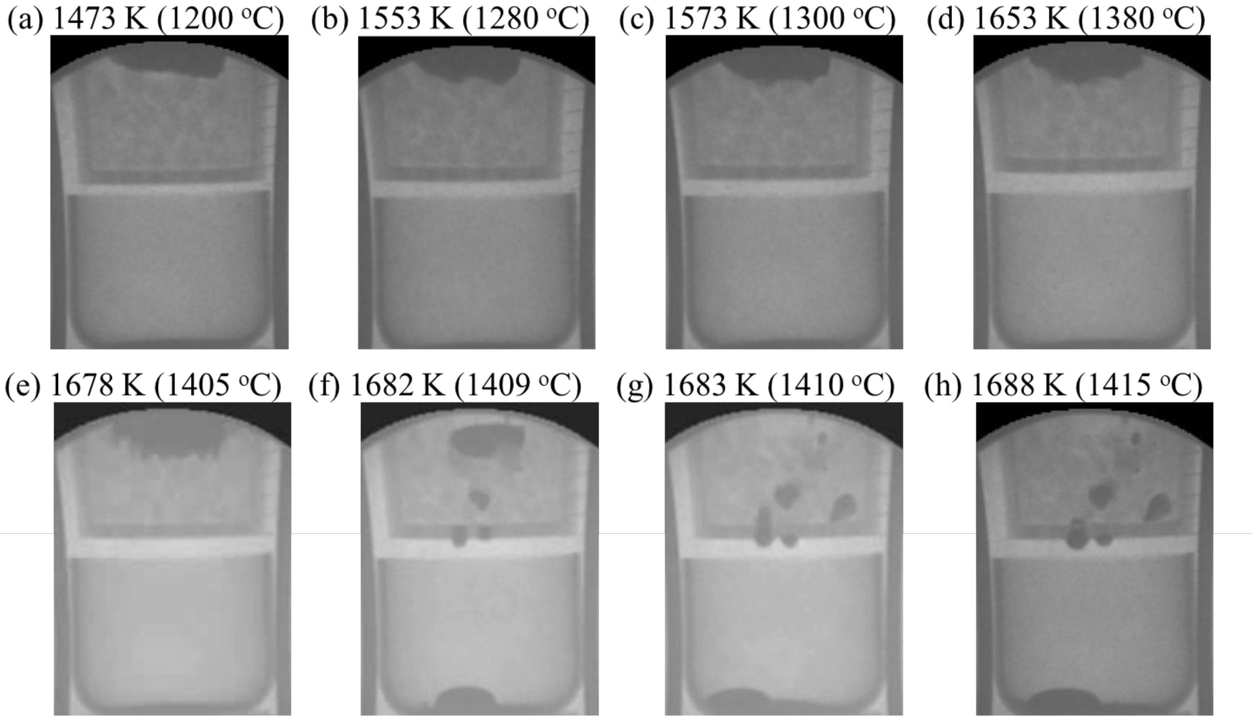

FIG 4 – In-situ observation of liquid metal and liquid slag formation from HCI on a coke bed under CO gas atmosphere.

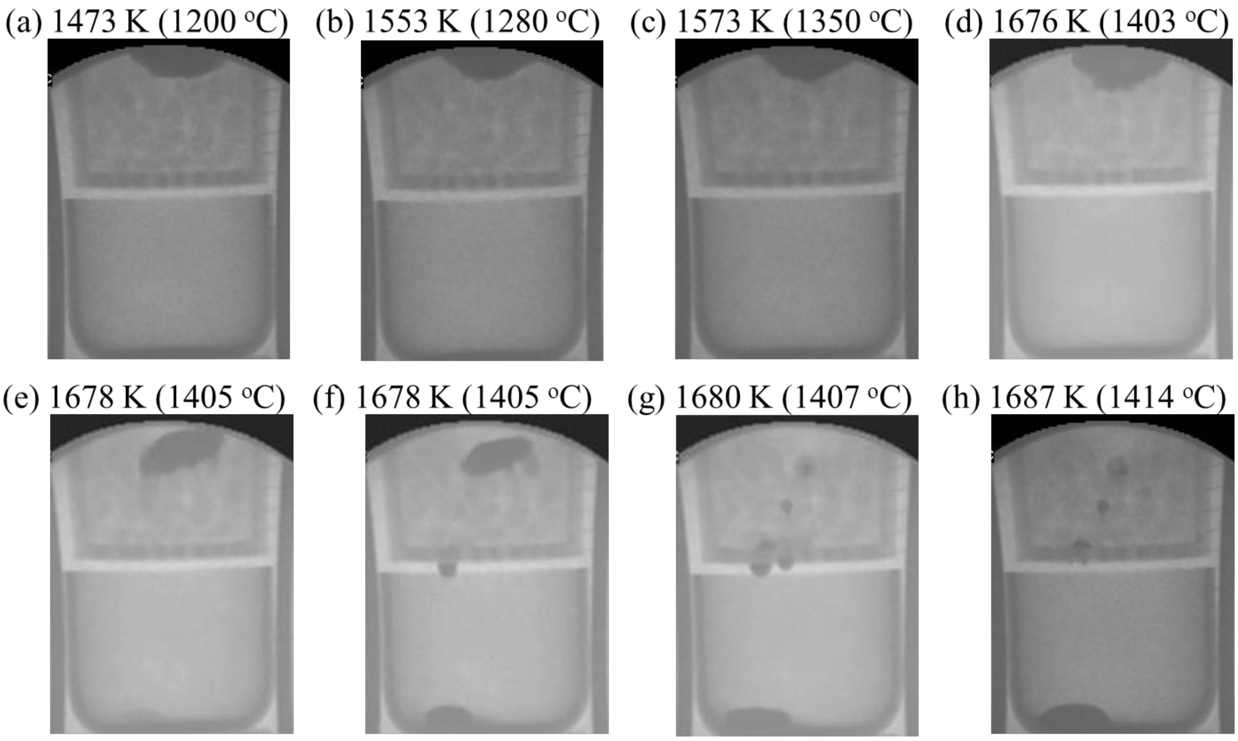

FIG 5 – In-situ observation of liquid metal and liquid slag formation from HCI on a coke bed under CO-20%H_2 gas atmosphere.

It is considered that the introduction of H_2 gas decreased FeO content in the slag, yielding the increased melting temperature of the slag as well as the slag viscosity [Park 2023a]. On the other hand, H_2 gas accelerated the carburization of the reduced iron, enabling the homogenization of the oxide materials to form a liquid phase [Oh 2017]. Therefore, it is considered that a reasonable introduction of H_2 in the blast furnace of the FINEX melter-gasifier is helpful to increase productivity and energy efficiency by accelerating the liquid phase's formation.

The slag holdup is affected by the particle size of the coke and thermophysical properties of liquid slag, such as density, surface tension, viscosity, and wettability [Jang 2012a], [Dereje 2021], [Dereje 2020]. In the practical blast furnace or FINEX melter-gasifier operations, the formation of the SiC layer would reduce the slag holdup by drastically modifying wettability [Kim 2023], [Oh 2016]. Therefore, the increased slag holdup investigated in this study would be reduced by the introduction of H_2 gas. Hence, the H_2-injecting ironmaking process would be more favorable for the establishment of an energy-efficient ironmaking process [Park 2023a].

In this study, however, detailed critical analysis, such as microstructure analysis of the sample and phase identification, was not carried out because the slag composition was changed by the reaction with the crucible. More sophistical experimental design is anticipated in future work.

CONCLUSIONS

The reduction, carburization, melting, and dripping behavior of HCI was investigated under a CO-H_2 gas mixture with the high-temperature X-ray radiographic technique. Fig. 6 shows the summary of the experimental results. Under 100% CO gas atmosphere, the dripping temperature was 1410°C. When 5% H_2 was introduced, the dripping temperature slightly decreased to 1400°C. As the H_2 gas composition increased further, the dripping temperature gradually increased. The carbon concentration in the drained metal samples gradually increased with increasing H_2 composition. It is considered that H_2 decreased FeO content in the slag, yielding the increased melting temperature of the slag, while it also accelerated the carburization of the reduced iron by CO gas, enabling the homogenization of the oxide materials to form a liquid phase. It is considered that a reasonable introduction of H_2 in the reactor is helpful in increasing productivity and energy efficiency by accelerating the liquid phase's formation.

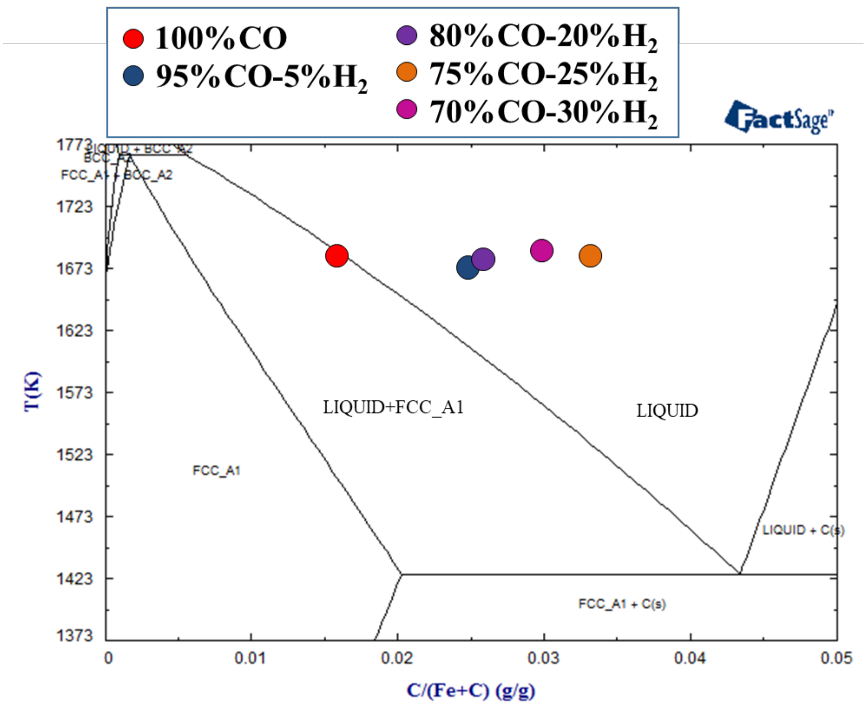

FIG 6 – Dripping temperature with respect to the carbon concentration of the dripped metal under various gas atmosphere.

ACKNOWLEDGEMENTS

This work was supported by the Industrial Strategic Technology Development Program (RS-2023-00262421, Development of basic design technology for hydrogen based ironmaking), funded by the Ministry of Trade, Industry & Energy in the Republic of Korea.

REFERENCES

[Dereje 2021] Dereje Degefa Geleta, Joonho Lee, "Analysis of the wettability effect on slag holdup in a fixed bed of carbonaceous particles using CFD–DEM simulations", Metallurgical and Materials Transactions B, vol.52, 2021, 2883–2891. https://doi.org/10.1007/s11663-021-02249-9

[Dereje 2020] Dereje Degefa Geleta, Md Irfanul Haque Siddiqui, Joonho Lee, "Characterization of Slag Flow in Fixed Packed Bed of Coke Particles", METALLURGICAL AND MATERIALS TRANSACTIONS B-PROCESS METALLURGY AND MATERIALS PROCESSING SCIENCE, Vol. 51, Issue 1, Feb. 2020, pp.102-113. https://doi.org/10.1007/s11663-019-01750-6

[Dereje 2018] Dereje Degefa Geleta, Joonho Lee*, "Effects of Particle Diameter and Coke Layer Thickness on Solid Flow and Stress Distribution in BF by 3D Discrete Element Method", Metall. Mater. Trans. B, 2018, vol.49, 3594-3602. https://doi.org/10.1007/s11663-018-1368-7

[Fruehan 1973] R.J. Fruehan, Metall. Trans. 4, 2123 (1973). https://doi.org/10.1007/BF02643276

[IEA 2020] IEA, Iron and Steel Technology Roadmap (IEA Publications, 2020). https://www.iea.org/reports/iron-and-steel-technologyroadmap. Accessed 29 Sept 2023.

[Jang 2012a] Dongik Jang, Minsoo Shin, Joon Seok Oh, Hyun-Soo Kim, Sang Ho Yi, Joonho Lee, "Static Holdup of Liquid Slag in Carbonaceous Beds", ISIJ Int., vol.54, June 2014, 1251-1255.

[Jang 2012b] Dongik Jang, Yunkyum Kim, Minsoo Shin, Joonho Lee, "Kinetics of carbon dissolution of coke in molten iron", Met. Mater. Trans. B, vol.43, December 2012, 1308-1314.

[Jeong 2013] In-Hyeon Jeong , Hyun-Soo Kim, Yasushi Sasaki, "Trickle Flow Behaviors of Liquid Iron and Molten Slag in the Lower Part of Blast Furnace", ISIJ Int., 2013, vol. 53, p. 2090-2098. https://doi.org/10.2355/isijinternational.53.2090

[Kim 2023] Mintae Kim, Sangho Jeon, Junwoo Park, Jiwoo Park, Moo-Eob Choi, Joonho Lee, "Investigation of SiC formation on the graphite surface by CO-H2-SiO gas", Journal of Materials Research and Technology, Volume 26, 2023, Pages 5373-5382, ISSN 2238-7854, https://doi.org/10.1016/j.jmrt.2023.08.238

[Kim 2001] H.S. Kim, S.H. Lee, Y. Sasaki, ISIJ Int. 50, 71 (2001). https://doi.org/10.2355/isijinternational.50.71

[Lan 2020] C. Lan, S. Zhang, X. Liu, Q. Lyu, M. Jiang, Int. J. Hydrog. Energy 45, 14255 (2020). https://doi.org/10.1016/j.ijhydene.2020.03.143

[Lee 2007] J. Lee, A. Tazuke, T. Tanaka, J.-H. Park, "Estimation of sulfur segregation at the interface between molten iron and graphite substrate from wetting experiments", Metals and Materials International, 15, 3, June (2009), 501-505.

[Long 2016] H.M. Long, H.T. Wang, W. Zhao, J.X. Li, Z.G. Liu, P. Wang, Ironmak. Steelmak. 43, 450 (2016). https://doi.org/10.1080/03019233.2015.1108480

[Nakamoto 2004] Masashi Nakamoto, Toshihiro Tanaka, Joonho Lee and Tateo Usui, "Evaluation of Viscosity of Molten SiO2-CaO-MgO-Al2O3 Slags in Blast Furnace Operation," ISIJ Int., Vol.44, No.12 (2004) 2125-2129.

[Oh 2017] Joon Seok Oh, Jaehong Lee, Joonho Lee, "Effect of Additive Size on Softening and Melting Behavior of Slag", Korean J. Met. Mater.,2017, vol.55, no.8, 566-571. https://doi.org/10.3365/KJMM.2017.55.8.566

[Oh 2016] Joon Seok Oh, Joonho Lee, "Composition-dependent reactive wetting of molten slag on coke substrates", J. Mater. Sci., vol. 51, 2016, 1813-1819. https://doi.org/10.1007/s10853-015-9588-6

[Park 2023a] Junwoo Park, Minki Kim, In-kook Suh, Eunju Kim, Joonho Lee, "Investigation of carburization and melting behavior of fully reduced LRI and IOS on coke substrates", Metals and Materials International, 2023, published online, https://doi.org/10.1007/s12540-023-01551-2

[Park 2023b] Junwoo PARK, Eunju KIM, In-kook SUH, Joonho LEE, "Effects of basicity and Al2O3 content on the crystal structure of silico-ferrite of calcium and aluminum", ISIJ International Vol. 63, No. 2. February 2023, 235-243. https://doi.org/10.2355/isijinternational.ISIJINT-2022-375

[Park 2022] Junwoo Park, Eunju Kim, In-kook Suh and Joonho Lee, "A Short Review of the Effect of Iron Ore Selection on Mineral Phases of Iron Ore Sinter", Minerals 12, (2022) 35. https://doi.org/10.3390/min12010035

[Park 2021] Junwoo Park, Hyeonwoo Park, Dereje Degefa Geleta, Wan Ho Kim, Joonho Lee, "In-Situ Observation of Slag Holdup in a Fixed Bed of SiC Particles Using High-Temperature X-ray Radiographic Technique", Metall Mater Trans B 52, (2021) 3561–3563. https://doi.org/10.1007/s11663-021-02295-3

[Park 2020] Junwoo Park, Ramaraghavulu Rajavaram, In-kook Suh, Jiwon Jeon, Sanghan Son, Joonho Lee, "Effects of basicity and Al2O3 content on the chemistry of phases in iron ore sinter containing ZnO", METALLURGICAL AND MATERIALS TRANSACTIONS B-PROCESS METALLURGY AND MATERIALS PROCESSING SCIENCE, Volume 51, Issue 6, December 2020, pp.3016-3027. https://doi.org/10.1007/s11663-020-01940-7

[Rajavaram 2016] Ramaraghavulu Rajavaram, Jaehong Lee, Joon Seok Oh, Han Gyeol Kim, and Joonho Lee, "Microwave Heating Characteristics of Magnetite Ore", Met. Mater. Int., 2016, vol.22, no.6, 1116-1120. https://doi.org/10.1007/s12540-016-6045-2

[Shin 2015] Minsoo Shin, Joon Seok Oh, Joonho Lee, "Carburization, Melting and Dripping of Iron through Coke Bed", ISIJ Int., vol. 55, No. 10, 2015, 2056-2063. https://doi.org/10.2355/isijinternational.ISIJINT-2015-115

[Shin 2014] Minsoo Shin, Joon Seok Oh, Jeoungho Lee, Sukkwang Jung, Joonho Lee, "Dissolution Rate of Solid Iron by Liquid Fe-C Alloy", Met. Mater. Int., vol. 20, No.6, Nov. 2014, 1139-1143. https://doi.org/10.1007/s12540-014-6018-2

[Shin 2012] Minsoo Shin, Soonki Min, Joonho Lee, Jin Gyun Park, Dong Joon Min, "In-Situ Observation of the Carburization of Solid Iron by Graphite", Met. Mater. Int., Vol.18, No.6, December 2012, 1041-1047.

[Shin 2010] Minsoo Shin, Seungyoun Cho, Joonho Lee, Joo-Hyun Park, "In-situ observation of dynamic interfacial phenomena between CaO(-SiO2 or Al2O3) slag and Fe-11%Cr alloy near the MgO-6%C refractory at 1823K", Met. Mater. Int., vol.16, no.3, June 2010, 495-499.

[Yi 2021] S.H. Yi, W.J. Lee, Y.S. Lee, W.H. Kim, Korean J. Met. Mater. 59, 41 (2021). https://doi.org/10.3365/KJMM.2021.59.1.41

[Yi 2019] SH Yi, ME Choi, DH Kim, CK Ko, W-I Park, SY Kim, "FINEX(R) as an environmentally sustainable ironmaking process", Ironmak Steelmak, 2019, vol. 46, 625e31. https://doi.org/10.1080/03019233.2019.1641682