Effects of Ash Amount and Molten Ash’s Behavior on Initial Fe–C Liquid Formation Temperature due to Iron Carburization Reaction

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1. Introduction

Carbonaceous material has many important roles in ironmaking process as follows: energy source, reducing agent for iron oxide of iron ore, carbon source for iron carburization reaction etc. Although hydrogen as green energy has a big possibility for utilization in ironmaking process as alternate source for carbon, it cannot completely take over. One of the biggest reasons of this is iron carburization reaction. This reaction cannot occur without carbon source. In other words, effective carbon source for iron carburization reaction is necessary to reduce carbon consumption in ironmaking process.

It is thought an enhancement of the iron carburization reaction directly means thinning of coke layer. This is a severe situation for liquid permeability around cohesive zone in blast furnace. The smooth separation from cohesive zone and dripping of molten iron need a quick formation of Fe–C liquid from lower temperature. This is one of the reasons there is strong demand for enhancement of the iron carburization reaction.

Various investigations about iron carburization reaction in ironmaking process have been reported. It has been generally considered that sources of carburization reaction are coke which has direct contact with metallic iron and carbonaceous gas surrounding there. Comparison of reaction kinetics of both carbon sources showed that the carburization by direct contact is dominant. This means that enhancement of carburization reaction needs high quality carbonaceous material for the reaction by direct contact.

In our previous study, it was found that carbon structure has clear effect on iron carburization reaction. The result indicated that low crystallinity of carbon has an advantage for this reaction. Additionally, it is thought that ash in carbonaceous materials has a strong effect on carburization reaction. There were many reports, which focused on effect of the ash on this reaction. However, their discussions...
were based on comparison among different kinds of carbon sources; coke, coal, graphite, etc. In other words, they could not exclude effects from other factors, especially carbon crystallinity. In order to focus on ash effect without change of carbon crystallinity, ash removal treatment to charcoal was applied in our previous work. The result showed clear effect of ash on iron carburization though charcoal is basically known as carbonaceous material with low ash content.

In order to clarify a mechanism of effect from carbonaceous material’s ash on the iron carburization reaction, effect of the ash amount and effect of the ash’s melting behavior were investigated in this study.

2. Experimental Methodology

In order to investigate about effect of carbonaceous material’s ash on iron carburization reaction at initial stage, Fe–C primary melt formation due to carburization reaction with constant heating rate condition under inert atmosphere was directly observed in this study.

4 kinds of carbonaceous materials were prepared in this study. Graphite powder was prepared as without ash containing carbon sample. As high amount ash containing sample, metallurgical coke powder was used. 2 kinds of charcoal powders were contained lower amount of ash content in there than the coke. All of them was grinded and sieved in order to control their particle diameter size between 45–75 μm.

The coke and the charcoal powders were soaked into HCl solution and HF solution during predetermined time for ash removal treatment. Residues amount of ash were measured by gravimetric measurement after combustion at 1 088 K under air atmosphere as JIS M 8812. The residues amounts of ash after the acid treatment were dependent on duration of this treatment as shown in Fig. 1.

Ash compositions before and after the treatment were evaluated by X-Ray Diffraction (XRD), Multiflex of Rigaku, and X-Ray Fluorescence Spectrometry (XRF), EDX-800HS of Shimadzu.

Figure 2 shows XRD patterns of the ashes. A collecting of charcoal’s ash residue had a big difficulty because the amount of residue was quite small. From this reason, only variation of coke’s ash composition could be evaluated. From comparison of coke’s ashes, it was thought that mineral phases in ash did not change through the acid treatment.

Table 1 shows estimated-compositions of ashes from results of XRF analysis in quinary system composition, CaO–SiO₂–Al₂O₃–Fe₂O₃–MgO, for coke and charcoal. It was found that charcoal included MgO component. Through the acid treatment, coke’s ash composition decreased Fe₂O₃ content and increased Al₂O₃ content. However, main component of coke’s ash, SiO₂, did not change before and after the treatment. From this stable trend of SiO₂ component and result of XRD, it was assumed that main component of ash could not change through the acid treatment. Alkali metals, Na, K etc., are generally well known as one of the minor components of ash. It was thought that they have obvious effects on ash melting behavior. In order to evaluate Na content of coke ash, Inductively-Coupled Plasma Atomic Emission Spectrometry (ICP-AES), ICPS-1000IV of Shimadzu, was additionally conducted for coke’s ashes in this study. Ashes of cokes before and after the treatment

Fig. 1. Relationships of each carbonaceous materials between ash residue amounts and acid treatment duration.

Fig. 2. X-ray diffraction patterns of ashes.
were dissolved into HCl and HF solution, and then the solutions were applied to ICP-AES analysis. From the result of ICP-AES, Na content in coke ash without the treatment was 0.519 mass% as Na$_2$O. In case of the ash with the treatment, Na could not be detected in this analysis. This change of Na content should have a big effect on coke ash melting behavior.

Coke ash melting behavior was directly observed using a laser microscope with infrared furnace.\cite{19} 5 mg of the ash was pressed into tablet shape (3 mm$\times$0.5 mm) by stainless dice. The ash tablet was put into Pt crucible (5 mm$\times$3 mm), and the crucible set on a Pt sample holder in the infrared furnace. Under Ar atmosphere, the sample was rapidly heated up to 1 323 K in 60 seconds, and then heated in constant rate of 50 K/min.

Main components of carbonaceous materials are generally fixed carbon, ash, and volatile matter. In previous works,\cite{9,18} it was found that carbon structure of fixed carbon has an obvious effect on carburization reaction. In order to focus on effects of ash and fixed carbon on the reaction, volatile matter of every material was removed by 3 600 seconds heat treatment at 1 273 K under Ar atmosphere in this study.

In the same way as in the previous work,\cite{9} carbon structures of the after-pyrolyzed samples were analyzed by a Raman spectroscopy, Xplora of Horiba, as shown in Fig. 3. These spectra have two peaks around 1580 cm$^{-1}$. The former and the latter peaks are known as G band and D band, respectively. G band is related to normal graphite structure. D band is originated from defect structure of graphite. And also, it is known that a peak, related to random structure, hide under valley between two peaks. For carbon structure evaluation in this study, intensity ratio between the valley and the G band, $I_V/I_G$, was applied and used for observation of initial Fe–C liquid formation behavior.

Table 1. Ash compositions of coke and charcoal evaluated by XRF (mass%).

|             | CaO  | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | MgO |
|-------------|------|---------|-------------|-------------|-----|
| Coke without acid treatment | 13.4 | 45.2    | 10.0        | 31.4        | —   |
| Coke with acid treatment     | 10.5 | 47.4    | 27.1        | 15.0        | —   |
| Oak’s charcoal                | 76.06| —       | 0.75        | 5.43        | 17.8|
| Eucalyptus’s charcoal         | 44.4 | 3.39    | 5.33        | 8.12        | 38.7|

In order to roughly evaluate a wettability of molten ash to iron and carbon, ash melting behaviors on iron and graphite substrate were observed, respectively. The iron thin plate, applied to iron carburization experiment, was used as iron substrate. A graphite plate was polished and applied as carbon substrate. Ash samples were prepared from coke ash with and without acid treatment. The ash samples were

![Fig. 3. Raman spectra of carbonaceous materials with $I_V/I_G$ values.](image3)

![Fig. 4. Schematic illustration and photograph of sample for direct observation of initial Fe–C liquid formation behavior.](image4)
pressed into tablet shape, 3 mm diameter and 1 mm height, each 15 mg. The ash tablet was put on the iron and the carbon substrate and set into alumina crucible. The samples were rapidly heated up to 1 473 K in 60 s and held 120 s then quenched in same way as the iron carburization experiment.

3. Results & Discussions

Figure 5 shows sequential laser micrographs obtained from “in-situ” observation of iron carburization reaction. At First, change of the iron sample’s surface occurred due to initial liquid formation of Fe–C. Then, amount of the liquid Fe–C was gradually increasing on the iron sample. An observed temperature of initial Fe–C liquid formation behavior on the iron sample was defined as initial liquid formation temperature due to iron carburization reaction in this study.

Relationship between ash content in carbon samples and this liquid formation temperature was shown in Fig. 6. It was indicated that carbon samples of lower ash content formed Fe–C liquid from lower temperature. And also, there was a clear effect of carbon structure difference among 4 kinds of carbon samples.

Figure 7 shows a dependency of the temperature on carbon structure. Results of lowest ash content plots of each carbon samples were picked up from Fig. 6 for this figure, because it could be made easy to focus on effect of carbon structure. Horizontal axis values, $I_V/I_G$, mean imperfection degree of graphite structure in the carbon samples. It was found that carbon samples of lower crystallinity formed Fe–C liquid from lower temperature as reported in previous works.9,18)

These results indicated that to make low both of carbon crystallinity and ash content is important to select a proper carbonaceous material for enhancement of iron carburization by direct contact.

Temperatures of initial ash’s melts formation were measured from these observations as shown in Fig. 8. It was found that the temperature was increased from 1 413 K to 1 457 K after the acid treatment. In Fig. 9, variation of liquid phase ratio was calculated using FACTSAGE21) when Na content decreases from coke ash component. At this calculation, several assumptions to focus on Na effect were applied as follows; the ash composition with acid treatment is estimated from Table 1 as quaternary system composition.

Fig. 5. Sequential laser micrographs of initial Fe–C liquid formation behavior between Fe plate and carbonaceous materials.

Fig. 6. Relationship between ash content in carbon samples and initial Fe–C liquid formation temperature.

Fig. 7. Relationship between $I_V/I_G$ value and initial Fe–C liquid formation temperature.
of CaO–SiO₂–Al₂O₃–Fe₂O₃, and the composition without acid treatment is decided as quinary system composition of CaO–SiO₂–Al₂O₃–Fe₂O₃–Na₂O by addition of 0.519 mass% Na₂O to the CaO–SiO₂–Al₂O₃–Fe₂O₃ composition with acid treatment. It was also indicated that decrease of Na content in ash has obvious effect on liquid formation temperature.

In order to investigate in detail about effect of ash behavior at the interface on iron carburization, samples were quenched at 50 K lower temperature from initial Fe–C liquid formation temperature on the iron samples. Figure 10 shows a comparison of cross-sectional photographs and results of EDS mapping analysis between acid treated coke and non-treated one. Although ash could not be found in this resolution at the cross-section of acid treated coke, ash particles were found at the interface of non-treated coke’s sample. It could be thought existence of ash at the interface decreased the reaction area between carbon and iron, and gave negative effect on carburization reaction. However, it might be not a dominant factor to obstruct the reaction because decreasing reaction area was not enough to explain this phenomenon. In Fig. 8, it was mentioned ash without acid treatment could be melted at lower temperature than the initial Fe–C liquid formation. The molten ash might have a negative effect on the carburization reaction due to the liquid barrier formation at the reaction interface.

Figure 11 shows photographs of after quenched samples.
Fig. 10. Comparison of cross-sectional photographs and results of EDS mapping analysis between acid treated coke and non-treated coke.

Fig. 11. Comparison of molten ash wettability to iron and graphite between with acid treatment and without acid treatment.

Non-treatment ash shows better wettability than ash with acid treatment on both kinds of substrates. It had been reported Na has obvious effects on not only melting temperature but also physical property of molten ash. Especially, surface tension of molten oxide has strong dependency on Na content.\textsuperscript{22–24} It was thought Na has effect to decrease surface tension of it.

Wetting behavior is considered as balance of surface tensions among solid, liquid, and their interface based on Young’s equation as shown in Eq. 1.

$$\sigma_{ls} = \sigma_{lg} + \sigma_{gs} \cos \theta \cdots \cdots \cdots \cdots (1)$$

where $\sigma_{ls}$, $\sigma_{lg}$, and $\sigma_{gs}$ are the interfacial energies between the liquid and solid, gas and liquid, and gas and solid, respectively. In this equation, contact angle changes to small value when liquid surface tension decreases. In other words, it can be thought decrease of liquid surface tension due to Na content in ash would cause improvement of wettability.\textsuperscript{25} Additionally, there is a possibility that interfacial surface tension could decrease due to reaction between molten ash and each solid phase. It has been reported that interfacial energy decrease when reaction could occur between liquid and solid phase.\textsuperscript{26} This variation of interfacial energy causes decrease of interfacial surface tension. As shown in Table 1, molten ash has many elements; they have possibilities of reaction against carbon. These contents should affect to improve wettability to carbon.

From these discussions, it was considered that ash could behave with and without acid treatment as shown in Fig. 12. In case of without acid treatment, molten ash could form at around 1 413 K before initial Fe–C liquid formation. The formed molten ash had a good wettability against
carbon and iron. It could cover on interface between carbon and iron. The molten ash might behave as a barrier of carburization reaction. In case of with acid treatment, molten ash could form at around 1,457 K after initial Fe−C liquid formation. The amount of formed molten ash could be small, and the molten ash could have weaker wettability than ash without acid treatment. From these reasons, molten ash could not work well as the barrier. Although there was possibility that Na content could decrease during heating experiment, it was considered that the amount of decreasing was quite small because heating times were short as less than 5 minutes and achieving temperatures were lower than 1,500 K, in this experimental condition. In this discussion, the decreasing effect of Na content during heating experiment was ignored from above reason.

From this study, it could not clarify contribution ratio to iron carburization reaction between amount of ash content and molten ash physical properties. Although it should be studied more in detail at near future, there is big possibility these factors strongly could affect also coal based DRI process because of their huge amount of reaction interface area due to utilization of pulverized carbonaceous materials.

4. Conclusions

Effects of amount and melting behavior of carbonaceous material’s ash on the iron carburization reaction were investigated by measurement of initial Fe−C liquid formation temperature using “in-situ” observation technique. Following results were obtained.

Decreasing of ash content in carbonaceous material decreased initial Fe−C liquid formation temperature because obstruction on reaction area of iron carburization reaction was decreased.

The acid treatment for decreasing of ash content in carbonaceous material decreased Na content of ash, too. This variation of Na content caused changing of molten ash’s properties, increasing of melting temperature and decreasing of wettability to iron and carbon.

In case of without the acid treatment, it was thought molten ash could behave as a barrier at a reaction interface of iron carburization due to good wettability from lower temperature than initial Fe−C liquid formation temperature.

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