

Effect of carbonaceous material graphitization degree on carburization behavior in Fe-C mixture powder during rapid heating

Ayana Ono^{1,*}, Tatsuya Kon², and Ko-ichiro Ohno² 

¹ Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395 Japan

² Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395 Japan

Received: 1 September 2025 / Accepted: 30 October 2025

Abstract. The transition to carbon-neutral steelmaking necessitates the development of alternative carburizing agents to replace fossil-derived carbon. This study investigates the effect of graphitization degree and ash content of biochar on the carburization behavior of Fe-C mixture powders during rapid heating. Carbonaceous materials with varying crystallinity and composition were prepared through heat treatment and acid leaching, and their structural disorder was evaluated using Raman spectroscopy (I_V/I_G ratio). Carburization behavior was examined using a laser microscope equipped with infrared image heating under controlled Ar-H₂ atmosphere. Two experimental approaches were applied: compact Fe-C pellets to determine complete melting temperature, and iron plate-carbon contact samples to observe the initial melt formation. Results showed that ash content, rather than graphitization degree, was the dominant factor influencing carburization. Ash-rich samples exhibited delayed and localized melt formation, while ash-removed biochar showed earlier and more uniform melting. The I_V/I_G ratio had limited correlation with melting behavior. These findings suggest that removing ash from biochar significantly enhances its performance as a carbon-neutral carburizing agent in hydrogen-based steelmaking routes such as H-DRI-EAF, offering a practical strategy for decarbonization in ironmaking.

Keywords: biochar / carburization / ash content / graphitization degree / Raman spectroscopy

1 Introduction

In the global pursuit of carbon neutrality, the steel industry is under increasing pressure to decarbonize its processes. Traditional steelmaking relies heavily on fossil-derived carbon sources such as coal and coke, which are not only non-renewable but also major contributors to CO₂ emissions. To reduce environmental impact, the use of carbon-neutral alternatives such as biomass-derived carbon materials has gained significant attention.

Among various biomass-derived carbon sources, biochar is particularly promising due to its low cost, wide availability, carbon neutrality, and compatibility with existing steelmaking infrastructure. However, its practical application requires a clear understanding of its behavior under high-temperature conditions, particularly during carburization—a process essential for adjusting carbon content in molten iron and facilitating melt formation.

Carburization efficiency is influenced by several properties of the carbonaceous material, including ash content, volatile matter, and crystallinity or graphitization degree. While previous research [1–8] suggests that low graphitization enhances reactivity due to increased structural disorder, other studies have emphasized the inhibitory effect of inorganic impurities, ash, on carbon-metal interactions. To develop effective carbon-neutral carburizing agents, it is necessary to disentangle the effects of crystallinity and ash content and to identify the dominant factors under practical heating conditions.

In this study, we examine the carburization behavior of iron-carbon mixtures using biochar samples with systematically varied ash content and graphitization degree. The behavior is assessed under rapid heating conditions, simulating realistic thermal histories such as those encountered in the hydrogen direct reduced iron, H-DRI, to electric arc furnace, EAF, pathway. Observations focus on melt formation behavior and its dependence on carbon structure and ash content

* e-mail: ono.ayana.115@kyushu-u.ac.jp

Table 1. Proximate analysis of samples (mass%).

		Composition of carbonaceous materials			
		C	VM	Ash	I_V/I_G
Charcoal	Raw	82.9	15.0	2.17	0.41
	Ash removed	84.3	15.0	0.69	0.45
	VM removed	97.4	–	2.55	0.30
	Ash removed _ VM removed	99.2	–	0.83	0.32
	Graphite	99.9	–	–	0.02

2 Method

This work investigates the carburization behavior of iron–carbon mixtures and carbon on Fe sheet by employing biochar samples with controlled variations in ash content and graphitization degree. The experiments were performed under rapid heating to replicate thermal histories typical of H-DRI to EAF route. Emphasis is placed on the melt formation process and its sensitivity to both carbon structure and ash.

2.1 Carbonaceous materials

Various biochar samples were prepared from commercial charcoal powders by applying post-treatments to modify their ash and volatile matter content. Heat treatment at 1450 °C under Ar atmosphere for 30 min was used to remove volatile matter and partially reorder the carbon structure. Ash was removed by sequential acid leaching with 18% HCl (aq) followed by 46% HF (aq) for 24 h each [1]. Graphite reagent-grade powder was used as a highly crystalline reference. All of them was grinded and sieved to control their particle size under 45 µm.

The graphitization degree was evaluated using Raman spectroscopy. The random structure index I_V/I_G , calculated as the decrease in intensity of the valley (the height of the minimum point) between the G and D bands [9]. Charcoal was categorized with fixed carbon, volatile matter, VM, and ash, with moisture content ignored, after drying the sample at 120 °C for 24 h. The proximate analysis of the charcoal is shown in Table 1. For evaluation of volatile matter amount, 1.000 g of sample was weighed, heated in a horizontal furnace under an Ar atmosphere at a rate of 100 °C/min to 1450 °C, and then heat treated at 1450 °C for 30 min. The weight loss during this heat-treatment was applied to calculate the volatile matter in this study. The de-VM temperature was determined based on the experimental temperature to prevent thermal decomposition during the heating process. The ash content was measured using the gravimetric method based on JIS M 8812. The measurement method is described below. Approximately 1.000 g of sample was weighed, placed in a platinum crucible. Using a muffle furnace, the sample was incinerated in air atmosphere by heating from room temperature to 500 °C over 1 h, then to 815 °C over 30 min, and holding at 815 °C for 30 min. The ash content was determined by weighing the ash residue and calculating its ratio to the initial weight.

2.2 Experimental setup

Figure 1 shows experimental setup. Carburization behavior was investigated using a laser microscope integrated with an infrared image heating furnace. It is difficult to observe samples at temperatures exceeding 1200 °C using optical microscopes or high-temperature scanning electron microscopes due to the significant influence of radiation from the samples. Therefore, by adopting a system combining a confocal scanning laser microscope with an infrared imaging furnace, we enabled “*In situ*” observation of the behavior of various materials at high temperatures.

The observation light source uses a He-Ne laser (632.8 nm, 1.5 mW). The laser’s coherence enables focusing into a minute area (beam diameter approx. 0.5 µm), achieving high brightness. The adoption of a confocal optical system blocks unwanted scattered light from outside the focal position via a pinhole in front of the CCD. However, since only a micro-spot of approximately the same size as the beam diameter can be observed, light beam scanning is performed to observe a wide area of the sample and to create images using the confocal optical system. Two experimental configurations were employed:

- **Experiment 1:** The compact bodies which consist of Fe-C mixture powder, $\Phi 7$ mm $\times$ 1 mm, 4 mass% carbon, were heated to assess the complete melting temperature.
- **Experiment 2:** Thin iron plates (3 $\times$ 3 $\times$ 0.1 mm) were placed in direct contact with carbon powder samples to observe the initial melt formation temperature.

Heating was performed under a constant flow of high purity Ar gas (0.3 NL/min) in experiment 1. Ar–H₂ mixed gas (0.3 NL/min) used in experiment 2 to prevent oxidation of the iron sheet. The samples were rapidly heated from room temperature to 800 °C at 1000 °C/min, then to 1400 °C at 100 °C/min. “*In-situ*” observation was performed during the heating process. After the heating experiment, the sample surface was provided to an optical microscope observation. Furthermore, in Experiment 2, observations of the iron sheet surface were conducted using SEM-EDS.

3 Results and discussion

3.1 Effect of graphitization degree

Figure 2 shows the relationship between the I_V/I_G ratio and the complete melting temperature in Experiment 1. Figure 3 shows the schematic diagram of the direct

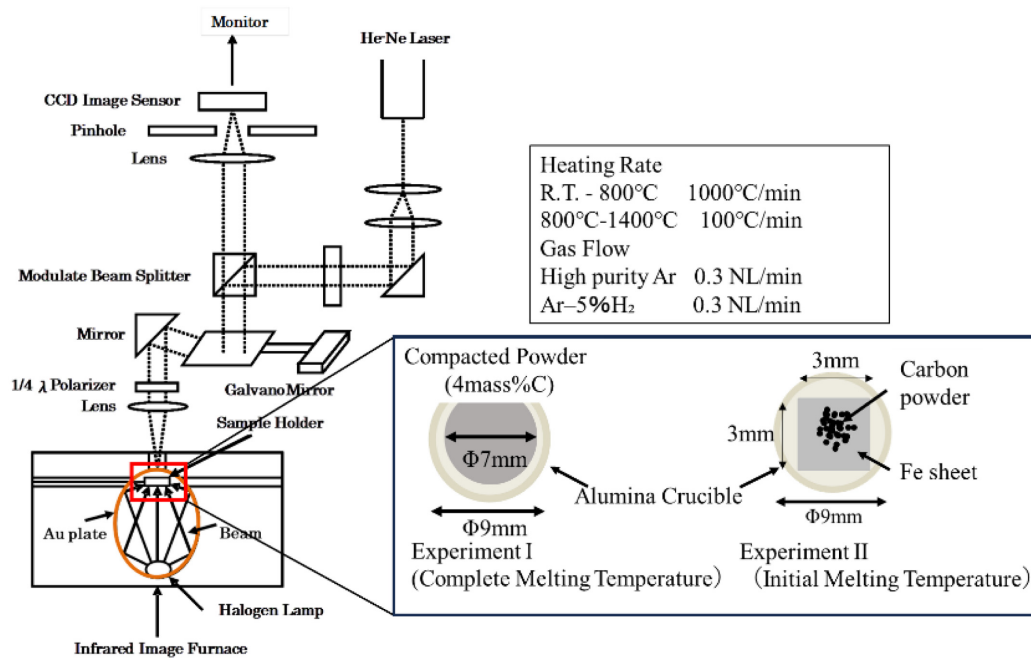


Fig. 1. experimental setup.

observation results. The definition of complete melting temperature in Experiment 1 is the point at which, when observing the tablet's upper surface with a laser microscope, the tablet aggregates and becomes spherical during melting, and the resulting Z-axis focus shift is no longer detectable. Several previous studies [1,2] have reported that carbonaceous materials with low graphitization exhibit good carburizing properties. Although graphite had the lowest I_V/I_G value as 0.02 and about 20 K lower melting temperature than the raw or VM removed biochar, obvious effect was not observed among the biochar samples with intermediate I_V/I_G values within 0.30–0.45. This suggests that under rapid heating, the graphitization degree has a limited effect on the temperature at which melting of the Fe–C mixture occurs. Under rapid heating conditions, the minimal effect of graphitization degree on carburization is thought to arise because the difference in inter-carbon BDE due to graphitization degree [10,11] is sufficiently small compared to the energy input during rapid heating, the maximum output of the halogen lamp heat source is 1500W.

3.2 Role of ash content

Microscopic observation revealed that ash might act as a physical barrier, preventing carbon dissolution into iron and inhibiting spreading of the molten phase. This observation is reinforced by the results shown in Figure 4, which is comparison of the initial melting temperature among ash-removed samples, includes graphite. Figure 5 shows examples of “*in situ*” observation results obtained from Experiment 2. (A) shows the initial heating stage of the sample, (B) shows the transition from a heating rate of 1000 °C/min to 100 °C/min. Subsequently, (C) confirms the initiation of molten iron sheet formation in the area circled in white. The point in (C) was defined as the initial molten sheet formation temperature in Experiment 2.

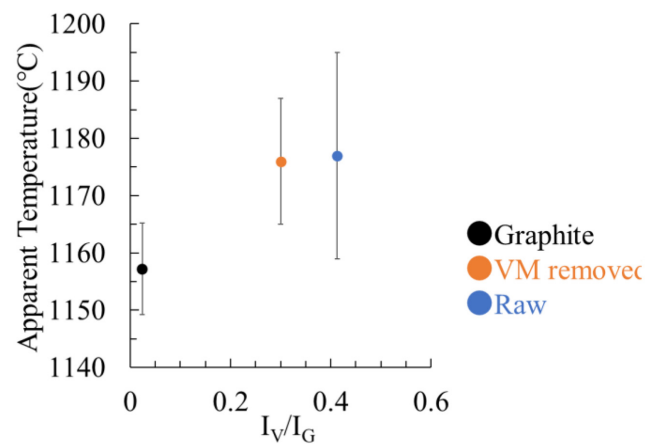


Fig. 2. Relationship between complete melting temperature and I_V/I_G in Experiment 1.

Although the temperature at which melt formation occurs is low, since this study is based on direct observation via video, this temperature was defined as the initial melt temperature. The cause of melting below the eutectic temperature is assumed to be differences between the actual experiment and the temperature compensation setup, along with variations in infrared heating due to sample color. In the actual experiment, carbonaceous material was placed in contact with an iron plate. However, for temperature compensation, Ag, Cu, and Ni powders were placed directly into the crucible. After creating the temperature compensation formula, further temperature compensation was performed using Ag, which does not react with iron, in the same setup as the actual experiment. The temperature difference between calibration samples with and without the iron plate may be attributed to

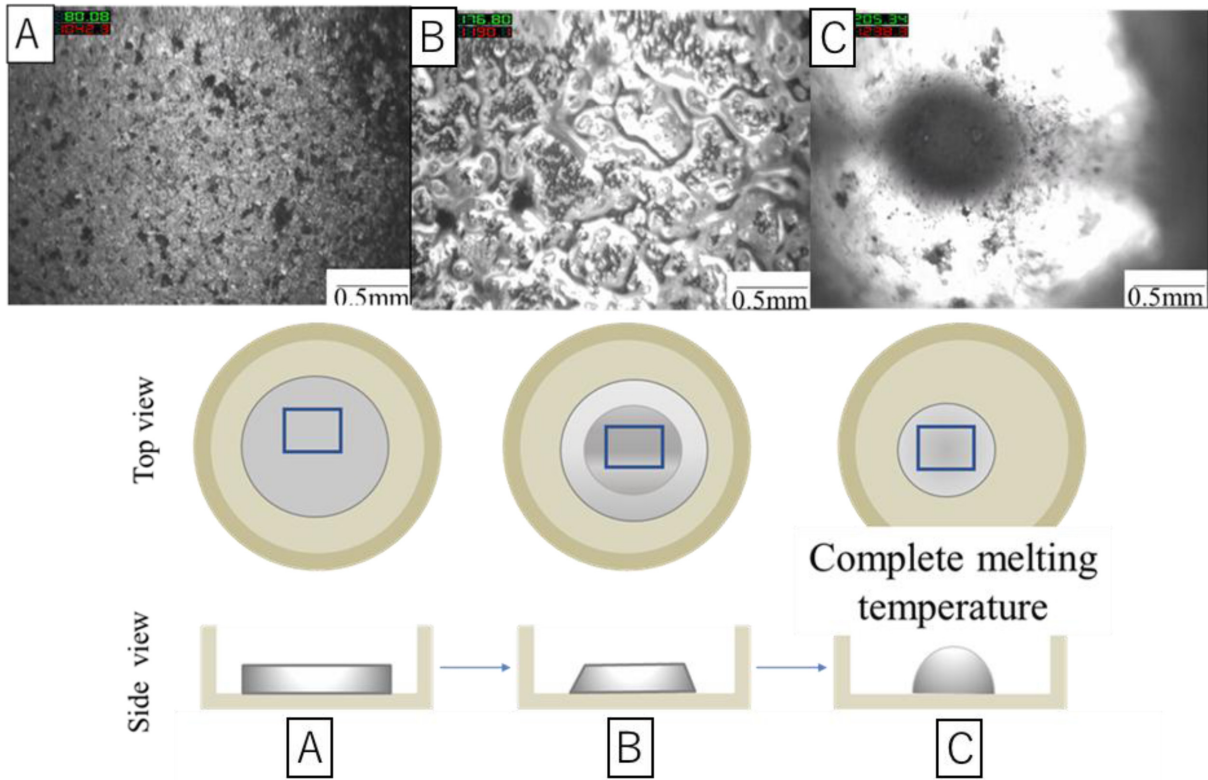


Fig. 3. Schematic image of melting behavior of compacted powder during heat process.

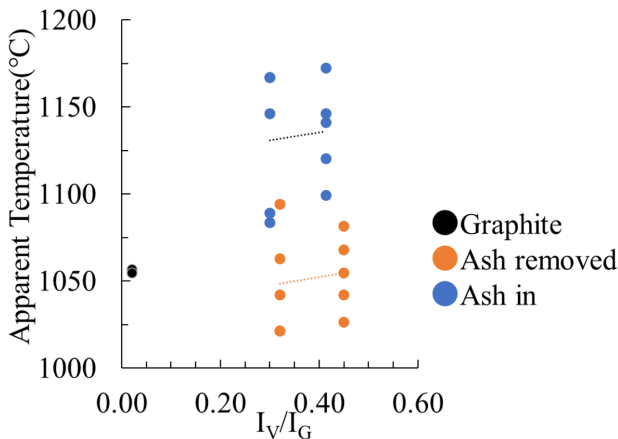


Fig. 4. Relationship between initial melting temperature and I_V/I_G in Experiment 2.

infrared radiation reflected by the plate potentially being reused to heat the sample. Furthermore, the carbonaceous material used in the actual experiment is black, meaning it has a higher infrared absorption rate than the metal sample used for temperature correction, making it easier to heat up. These factors might explain why the initial melt formation appeared to occur below the eutectic point temperature. Even when the graphitization degree remained constant, a lower ash content led to lower melt initiation temperature. Figure 6 shows the relationship

between initial melt formation temperature and ash content in Experiment 2. The initial melt formation temperature increased as the ash content increased.

Figure 7 shows the optical microscope observation results of the molten iron formation area on the surface of the iron sample after the experiment. In charcoal samples without ash removal treatment, structures resembling ash were observed on the surface of the molten pool formation area. In graphite samples, numerous crystal phases suggesting the precipitation of carbon or carbides after cooling were observed. The presence of ash on the molten surface likely hindered contact among the formed molten iron pools, the spreading of the molten iron, and contact between the charcoal and the iron plate.

The results of EDS mapping analysis for the iron sheet surfaces are shown in Figure 8. In charcoal without ash removal treatment, a structure resembling ash was observed on the surface of the molten iron formation area. As the carburization reaction progressed, ash from the charcoal material accumulated at the interface between the steel plate and the carbonaceous material, forming a physical barrier that impeded contact between the carbonaceous material and the steel plate as shown in Figure 9.

3.3 Additional observations

In Experiment 2, visual changes in the carbon material and iron plate were noted at characteristic temperatures. Figure 10 shows examples of “*In situ*” observation results using a laser microscope in Experiment 2. Around 500°C,

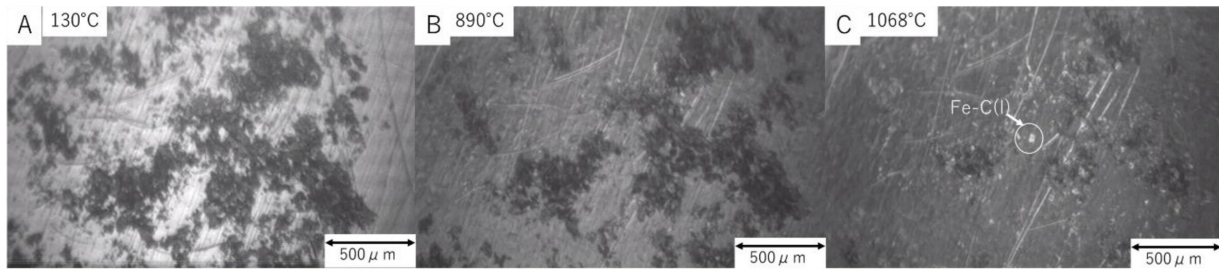


Fig. 5. Laser micrographs of melting behavior of Fe sheet.

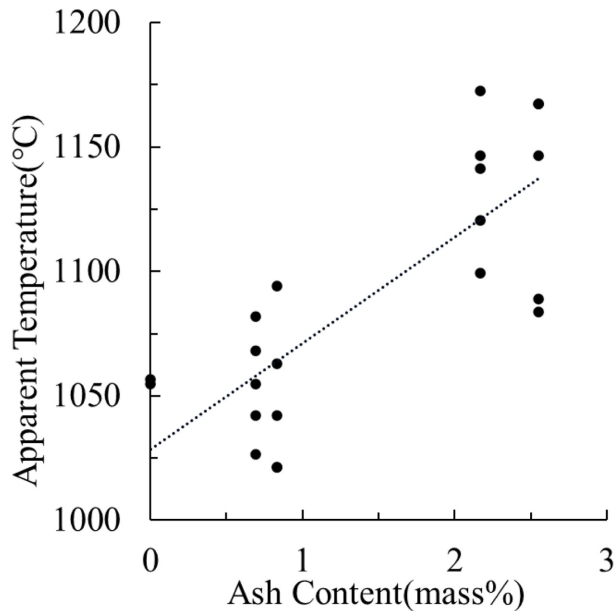


Fig. 6. Relationship between initial melt formation temperature and ash content in Experiment 2.

movement in the carbon particles suggested early onset of solid-state interfacial reactions. At approximately 900 °C, color and morphology changes in the iron plate were consistent with austenite transformation, after which carbon uptake accelerated [12].

The laser microscope experiments observed carburization behavior under rapid heating conditions using a setup with minimal contact points between carbonaceous material and iron. Detailed measurements were performed using Differential thermal analysis, DTA, under a setup with slow heating rates and numerous contact points between carbonaceous material and iron. Figure 11 shows the result of DTA. The melting onset for ash-removed biochar was 1174.5 °C, compared to 1179.5 °C for raw biochar—despite similar I_V/I_G values. These differences underscore the dominant role of ash content in carburization under practical conditions.

3.4 Implications for carbon-neutral steelmaking

The findings have clear implications for the practical use of biomass carbon in steelmaking:

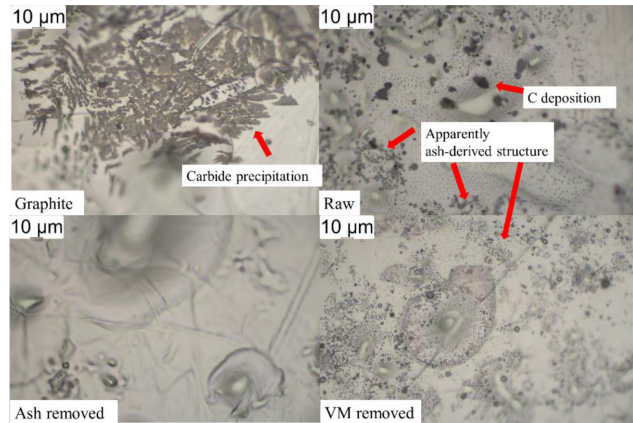


Fig. 7. Optical microscope observation of samples surface after experiments.

- **Carbon selection:** Biochar is a viable alternative to fossil carbon, but its performance strongly depends on its ash content.
- **Pretreatment importance:** Acid leaching or other ash-removal techniques are essential to unlock the full carburization potential of biochar.
- **Process compatibility:** Under rapid heating like EAF or induction furnace conditions, crystallinity is less critical than previously assumed, simplifying material selection.

These insights support the use of refined biomass-based carbon additives in hydrogen-based steelmaking routes, especially for applications where controlled carburization and melt formation are required—such as refining H-DRI in EAFs or adjusting the carbon content during decarbonized hot metal processing.

4 Conclusion

This study systematically evaluated the carburization behavior of Fe–C mixtures using biochar and graphite under rapid heating. While graphitization degree, represented by the I_V/I_G ratio, showed minimal influence on melt formation, ash content was found to be a critical factor. Lower ash content promoted earlier and more extensive melting, even at similar levels of carbon crystallinity.

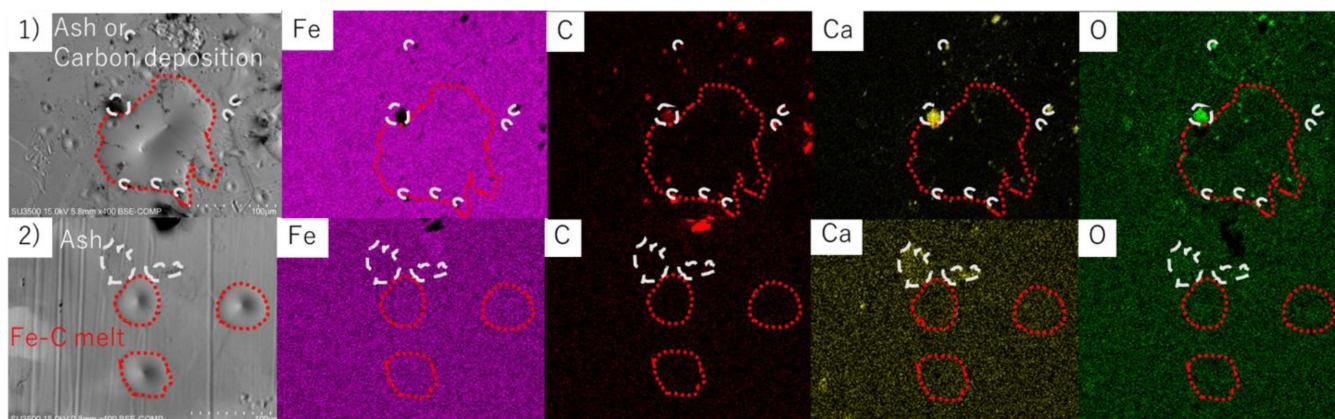


Fig. 8. Backscattered electron (BSE) images of 1) Raw Charcoal, 2) Ash removed VM removed Charcoal and compositional maps for Fe, C, Ca and O with color superposition (Fe = magenta; C = red; Ca = yellow; and O = green).

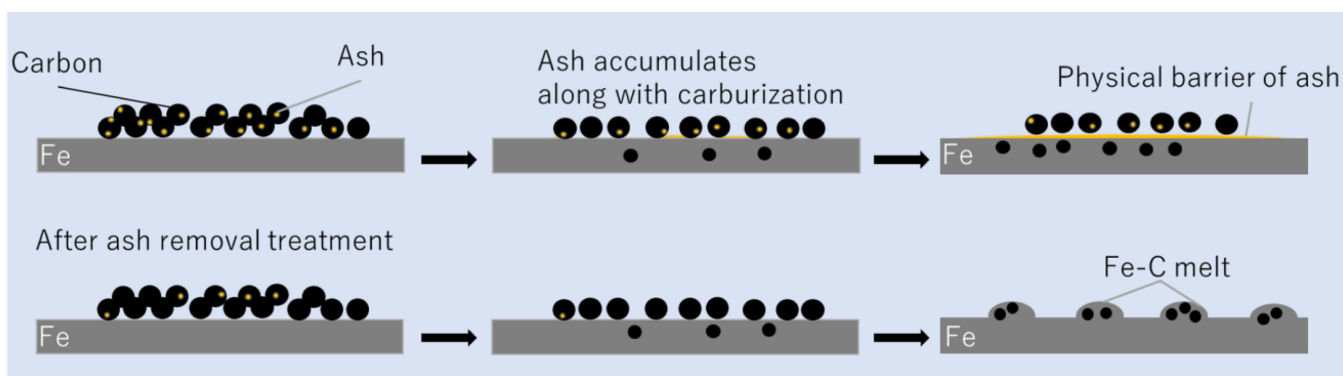


Fig. 9. Schematic image of how to work ash content as physical barrier which prevent carburization.



Fig. 10. Laser microscope image of carburization behavior during the heating process in Experiment 2: A,B) Circles of the same color are the same size.

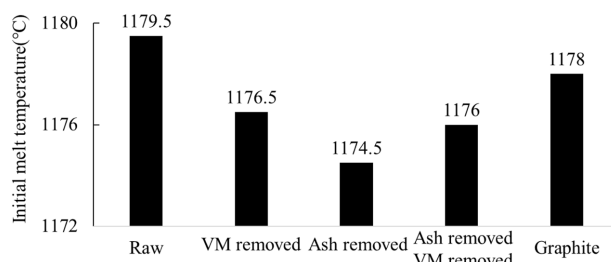


Fig. 11. Initial melt formation temperature of each sample in DTA.

These results suggest that for practical applications in carbon-neutral steelmaking, efforts should focus on ash reduction rather than enhancing graphitic order. This approach simplifies the development and deployment of biochar-based carburizers in emerging low-carbon steel production systems.

Funding

This research received no external funding.

Conflicts of interest

The authors declare that there are no conflicts of interest.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author contribution statement

The research was conceived and supervised by Ko-ichiro Ohno. Tatsuya Kon developed the experimental methodology and assisted with data analysis.

Ayana Ono performed the experiments and prepared the initial manuscript draft.

The manuscript was reviewed and edited by Ko-ichiro Ohno and Tatsuya Kon.

All authors have read and approved the final version of the manuscript.

References

1. K. Ohno, A. Babich, J. Mitsue et al., Effects of charcoal carbon crystallinity and ash content on carbon dissolution in molten iron and carburization reaction in iron-charcoal composite, *ISIJ Int.* **52**, 1482 (2012)
2. K. Ohno, T. Maeda, K. Nishida et al., Effect of carbon structure crystallinity on initial stage of iron Carburization, *ISIJ Int.* **50**, 53 (2010)
3. Y. Tomita, K. Shimada, T. Ida, Carburizing effect of cast iron in high-frequency induction electric furnace melting by Bio-Coke, *Mater. Trans.* **66**, 645 (2025)
4. R. Robinson, L. Brabie, M. Pettersson et al., An empirical comparative study of renewable biochar and fossil carbon as carburizer in steelmaking, *ISIJ Int.* **62**, 2522 (2022)
5. K. Tsutsumi, T. Nagasakai, M. Hino, Surface roughness of solidified hnoru flux in continuous casting process, *ISIJ Int.* **39**, 1150 (1999)
6. Y. Kamei, T. Miyazaki, H. Yamaoka, Production test of high-carbon ferromanganese using a shaft furnace with coke packed bed injected with highly oxygen enriched air and a large quantity of pulverized coal, *ISIJ Int.* **33**, 259 (1999)
7. S.T. Cham, V. Sahajwalla, H. Sun et al., Factors influencing carbon dissolution from cokes into liquid iron, *ISIJ Int.* **44**, 1835 (2004)
8. S.T. Cham, R. Sakurovs, H. Sun et al., Influence of temperature on carbon dissolution of cokes in molten iron, *ISIJ Int.* **46**, 652 (2006)
9. M. Kawakami, T. Karato, T. Takenaka et al., Structure analysis of coke, wood charcoal and bamboo charcoal by Raman spectroscopy and their reaction rate with CO₂, *ISIJ Int.* **45**, 1027 (2005)
10. D.R. Lide, A survey of caron-carbon bond lengths, *Tetrahedron* **17**, 125 (1962)
11. S.L. Boyd, R.J. Boyd, P.W. Bessonette et al., A theoretical study of the effects of protonation and deprotonation on bond dissociation energies, *J. Am. Chem. Soc.* **117**, 8816 (1995)
12. D.E. Jiang, E.A. Carter, Carbon dissolution and diffusion in ferrite and austenite from first principles, *Phys. Rev. B* **67**, 214103 (2003)

Cite this article as: Ayana Ono, Tatsuya Kon, Ko-ichiro Ohno, Effect of carbonaceous material graphitization degree on carburization behavior in Fe-C mixture powder during rapid heating, *Metall. Res. Technol.* **123**, 203 (2026), <https://doi.org/10.1051/metall/2025116>