Ultrafast Iron-Making Method: Carbon Combustion Synthesis from Carbon-Infiltrated Goethite Ore

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Abstract: Carbon-infiltrated iron ores were prepared from a coal-tar solution and selected calcined iron sources (i.e., goethite (FeOOH) ore, high-grade hematite ore, and FeO reagent grain). A several hundred micrometer thick carbon layer was deposited on the surface of all iron sources. Because the tar solution successfully penetrated into its nanopores, only goethite ore possessed a significant amount of carbon in its interior nanopores. The carbon-infiltrated ores were heated rapidly in an oxygen atmosphere in the combustion synthesis experiments. Carbon combustion occurred at the ore surface, with the ore temperature increasing suddenly during the experiments. Fast reduction to metallic iron was observed only in the carbon-infiltrated goethite ore, regardless of the oxygen atmosphere. Close contact between the goethite ore and the carbon in its nanoporous interior facilitated the fast reduction. The apparent reduction reaction of goethite ore is akin to a direct reduction reaction (i.e., FeO + C → Fe + CO). Goethite ore are attainable using an impregnation method, in which the ore and tar are directly mixed and heated. Although such an attractive raw material can be produced from mildly calcined nanoporous goethite ore, the goethite ore in the actual iron-making process is heated with coke breeze and binder at temperatures greater than 1400 °C for 20 h to satisfy the demand of the BF, which destroys the nanoporous structure of the goethite ore. It is also possible to make iron via the attractive “combustion synthesis (CS)” method for carbon-infiltrated goethite ores with high carbon content. CS utilizes strong exothermic reactions to self-propagate the combustion wave to complete the reaction spontaneously; several different types of materials have been prepared by this method. For carbon-infiltrated goethite ore, the CS reaction consists of carbon combustion and the reduction of iron oxides. When the total reaction is strongly exothermic, the CS reaction will be self-propagating and rapidly reach completion. Overall, CS iron making using carbon-infiltrated goethite ore has several benefits: (i) the amount of required coke can be decreased, (ii) the reduction will be completed very quickly, and (iii) the product can be used not only as an iron source but also as a heat source for the melting process for separation from slag.

In this study, carbon-infiltrated iron ores were produced from coal tar-based liquid and selected iron sources, including nanoporous goethite ore. CS experiments were then conducted.

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ABSTRACT: Carbon-infiltrated iron ores were prepared from a coal-tar solution and selected calcined iron sources (i.e., goethite (FeOOH) ore, high-grade hematite ore, and FeO reagent grain). A several hundred micrometer thick carbon layer was deposited on the surface of all iron sources. Because the tar solution successfully penetrated into its nanopores, only goethite ore possessed a significant amount of carbon in its interior nanopores. The carbon-infiltrated ores were heated rapidly in an oxygen atmosphere in the combustion synthesis experiments. Carbon combustion occurred at the ore surface, with the ore temperature increasing suddenly during the experiments. Fast reduction to metallic iron was observed only in the carbon-infiltrated goethite ore, regardless of the oxygen atmosphere. Close contact between the goethite ore and the carbon in its nanoporous interior facilitated the fast reduction. The apparent reduction reaction of goethite ore is akin to a direct reduction reaction (i.e., FeO + C → Fe + CO). Goethite ore are attainable using an impregnation method, in which the ore and tar are directly mixed and heated. Although such an attractive raw material can be produced from mildly calcined nanoporous goethite ore, the goethite ore in the actual iron-making process is heated with coke breeze and binder at temperatures greater than 1400 °C for 20 h to satisfy the demand of the BF, which destroys the nanoporous structure of the goethite ore. It is also possible to make iron via the attractive “combustion synthesis (CS)” method for carbon-infiltrated goethite ores with high carbon content. CS utilizes strong exothermic reactions to self-propagate the combustion wave to complete the reaction spontaneously; several different types of materials have been prepared by this method. For carbon-infiltrated goethite ore, the CS reaction consists of carbon combustion and the reduction of iron oxides. When the total reaction is strongly exothermic, the CS reaction will be self-propagating and rapidly reach completion. Overall, CS iron making using carbon-infiltrated goethite ore has several benefits: (i) the amount of required coke can be decreased, (ii) the reduction will be completed very quickly, and (iii) the product can be used not only as an iron source but also as a heat source for the melting process for separation from slag. In this study, carbon-infiltrated iron ores were produced from coal tar-based liquid and selected iron sources, including nanoporous goethite ore. CS experiments were then conducted.

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to reduce the carbon-infiltrated iron ores, and the reaction mechanism was discussed in terms of the obtained results.

■ RESULTS AND DISCUSSION

Carbon-infiltrated iron ores were prepared from the goethite ore, the high-grade hematite iron ore, and the Fe$_2$O$_3$ reagent, which were precalcined in air. The goethite ore mainly composed of FeOOH before calcination and completely decomposed to Fe$_2$O$_3$ via the following dehydration reaction

$$2\text{FeOOH} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$$

For natural goethite ore, dehydration of FeOOH begins from 230 °C, leading to the formation of ~4 nm nanopores. Although nanopores exist after calcination at 800 °C, their specific surface areas decrease drastically by calcination at higher temperatures; temperatures of 230–400 °C are optimal for goethite ore calcination. The goethite ore used in this study was calcined under various conditions: 300 °C for 24 h, 500 °C for 1 h, 800 °C for 1 h, 1000 °C for 24 h, and 1200 °C for 24 h. The pore size distributions, Brunauer–Emmett–Teller (BET) surface areas, and pore volumes are shown in Figure 1. The pore size distributions were determined by the Barrett–Joyner–Halenda method. Pores smaller than ~2 nm and larger than ~4 nm were observed in the goethite ores calcined at 300 and 500 °C. According to Naono et al., two types of nanopores are existent in calcined goethite ore: larger pores (~4 nm) and smaller pores (~1 nm). Larger nanopores were already present between the primary particles in the original goethite ore, and they are comparatively stable against calcination. In contrast, the smaller nanopores formed during the decomposition reaction of goethite ore, and they became larger during calcination at higher temperatures. However, the smaller pores disappeared during calcination at 800 °C and a strong peak in the pore size distribution curve, corresponding to a pore size of 4 nm, was obtained. This result indicates that smaller pores grew up to ~4 nm during calcination at high temperature. Calcination at temperatures over 1000 °C completely destroyed the nanopores in the goethite ore. Thus, the goethite ore had three types of pore structures after calcination at different temperatures: (i) pores ~2–4 nm (300–500 °C), (ii) pores ~4 nm (800 °C), and (iii) no pores (1000–1200 °C).

For the carbon-infiltrated goethite ore, precalcination at 300 °C for 24 h gave rise to 24.4 mass % of elemental C after heat treatment with the tar solution. The ore also contained 0.64 mass % of elemental H, indicating that the tar solution did not completely decompose into carbon and that some of it was deposited in the form of hydrocarbons. Fe$_2$O$_3$ in the goethite ore was partially reduced to Fe$_3$O$_4$ after heat treatment with the tar solution at 500 °C. Figure 2 shows cross-sectional scanning electron microscopy (SEM) images and pore size distributions of the goethite ore after calcination at 300–1200 °C for 1 and 24 h.

Figure 1. (A) Pore distributions and (B) BET surface areas and pore volumes of the goethite ore after calcination at 300–1200 °C for 1 and 24 h.

Figure 2. Cross-sectional SEM–EDS images of carbon-infiltrated (A) goethite ore and (B) high-grade ore. The red areas in the EDS images correspond to elemental carbon.
pore size distributions of these ores indicate that the calcined goethite ore possessed more nanopores than the carbon-infiltrated one. These results strongly supported that carbon was successfully deposited into the nanopores of the calcined goethite ore.

The effect of nanopores on the reduction of iron oxides was observed by using different iron sources and by changing the precalcination conditions. Figure 4 shows the X-ray diffraction (XRD) patterns, compositions, and reduction degrees (RD) of the samples after these CS experiments. The compositions and the RD were determined for iron components using the reference intensity ratio method based on the XRD results. The RD was calculated using

$$RD = \frac{\text{mass of removed oxygen}}{\text{mass of removable oxygen in Fe}_2\text{O}_3} \times 100 \%$$

First, the effect of the type of raw material was examined. Carbon-infiltrated goethite ore, high-grade ore, and Fe$_2$O$_3$ reagent were subjected to CS conditions of 900 °C for 10 s under a 25 vol % O$_2$ atmosphere. These experiments confirmed that reduction proceeded to metallic iron only in the carbon-infiltrated goethite ore (sample 1); only Fe$_3$O$_4$ and Fe$_2$O$_3$ were observed in the high-grade ore (sample 2) and the reagent (sample 3), and reduction of the iron source to metallic iron proceeded only when the goethite ore was used. The goethite ore after calcination at lower temperatures had a nanoporous structure; the tar solution can easily infiltrate into the pores, resulting in extensive contact between the goethite ore and carbon. Hosokai et al. reported that nano-order contact between iron ore and carbon is very effective for reduction. They produced carbon-infiltrated iron ore from precalcined natural goethite ore and pyrolyzed biomass tar and reduced it under an inert atmosphere. As a result, the ore was reduced at lower temperature compared with the mixture of μm sized Fe$_3$O$_4$ reagent and carbon black or coke. The carbon-infiltrated goethite ore used in this study was reduced to iron through such nanocontacts. In the case of high-grade iron ore and Fe$_3$O$_4$ reagent, however, which did not have combined water (CW), poor contact was made between the iron oxides and carbon, thereby limiting metallic iron formation.

The effect of the nanopores was also investigated by changing the pore structure of the goethite ore under different calcination conditions (i.e., 300 °C for 24 h, 800 °C for 1 h, and 1000 °C for 24 h). As seen in Figure 1, different types of pores were obtained after calcination under these conditions. The reduction in the CS experiments proceeded to metallic iron only in the goethite ores precalcined at 300 and 800 °C (samples 1 and 4). As stated, this can also be understood in terms of the effect of nanocontacts between the goethite ore and carbon. Nanopores in the goethite ore were maintained...
only when the precalcination temperature was below 800 °C; carbon can be easily deposited in such nanopores, resulting in effective contact with the ore.

In addition, the effect of the atmosphere type was also investigated. Carbon-infiltrated goethite ores prepared from the goethite ore via calcination at 300 °C for 24 h were used for this purpose. The ores were heated at the same heating rate (of 20 °C s⁻¹) to 900 °C under oxygen (25 vol % O₂/Ar), argon (100 vol % Ar), and hydrogen (20 vol % H₂/Ar) atmospheres. The temperature was maintained for 10 s after reaching 900 °C, after that time the O₂ and H₂ gas flows were stopped. Surprisingly, reduction of the goethite ore proceeded more fully under the oxygen atmosphere (sample 1). In contrast, reduction proceeded only to Fe₃O₄ and partially to FeO under the argon (sample 6) and hydrogen (sample 7) atmospheres.

There was no difference in the reduction of the carbon-infiltrated goethite ore after the CS experiments under argon and hydrogen atmospheres. According to a previous report, hydrogen reduction of Fe₂O₃ to Fe₃O₄ occurs at 150 and 200 °C, whereas reduction of Fe₃O₄ to Fe begins at 400 °C. Under the oxygen atmosphere, the previously observed effect of hydrogen on the reduction of the goethite ore was not observed at all. This difference is attributed to the formation of a thick, dense carbon layer on the goethite ore surface (Figure 2), which prevented H₂ gas from contacting the goethite ore and reducing it.

Clearly, the highest degree of reduction must occur following carbon combustion at the ore surface. Figure 5 shows the temperature and temperature derivative of time during the CS experiments in oxygen (sample 1), argon (sample 4), and hydrogen (sample 5) atmospheres.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Temperature change and temperature derivative of time during the combustion synthesis experiments flowing 1 L min⁻¹ of 25 vol % O₂/Ar at 900 °C with a programmed temperature (black dotted line).

In the case of the argon and hydrogen atmospheres, the temperature was almost identical with the programmed temperature (black dotted line in Figure 5). However, the temperature suddenly increased in the oxygen atmosphere, reaching a maximum value of 1200 °C even though the temperature was set to 900 °C. This result demonstrates that carbon combustion occurred at the ore surface and that higher temperatures were obtained only in an oxygen atmosphere. Further, the results suggest that heat generated from the exothermic combustion reaction transferred to the goethite ore, promoting reduction reactions inside it.

Figure 6 shows the gas composition (i.e., O₂, CO, CO₂, H₂, H₂O, and CH₄) of the outflow gases during the CS experiments under an oxygen atmosphere. An increase in the amounts of CO, CO₂, and CH₄ and a decrease in the amount of O₂ were observed. The increase in CO₂ and the decrease in O₂ occurred simultaneously, indicating that O₂ consumption was caused by the combustion of carbon (C + O₂ → CO₂) at the surface of the carbon-infiltrated goethite ore. After several seconds from the onset of combustion, CO gas was generated, implying that it was produced by the direct reduction reaction between iron oxide and carbon (Fe₂O₃ + C → FeO + CO). Heat treatment under Ar atmosphere indicated that the direct reduction was dominant in the carbon-infiltrated goethite ore (Figure S3). The formation of CH₄ may be related to the decomposition of hydrocarbons. Elemental analysis revealed that the carbon deposited in the goethite ore was not pure C; the goethite ore contained 24.4 and 0.64 mass % of C and H, respectively. Some of the carbon were present as hydrocarbons and decomposed to C, CH₄, and other gases at high temperature.

The cross-sectional area of the goethite ore after the CS experiments in an oxygen atmosphere was observed using SEM–EDS and light microscopy (Figure 7). As seen, the thick carbon layer on the goethite ore surface, shown in Figure 2, disappeared due to carbon combustion. Detailed observation near the goethite ore surface revealed that red Fe₂O₃ was formed; reoxidation partially occurred where the carbon layer completely disappeared. The ore surface without the carbon layer easily contacted oxygen, resulting in fast oxidation. Clearly, a process to inhibit reoxidation is essential for carbon combustion synthesis iron making. The comparatively high Fe₂O₃ amounts in the samples 1 and 4, shown in Figure 4, should occur because of this reoxidation.

Figure 8 illustrates the work flow of the CS iron-making process using carbon-infiltrated goethite ore in this study. Mild calcination converted the goethite ore to nanoporous Fe₂O₃. Nanocontacts between the ore and carbon formed in the
carbon-infiltrated goethite ore because of the presence of nanopores. During the CS iron-making process, heat generated from the exothermic carbon combustion at the ore surface became the heat source for reduction, and the fast reduction of the goethite ore is attributed to nanocontacts between it and carbon embedded within its interior nanopores. In this study, metallic iron was partially obtained via the CS process, and the highest reduction degree was obtained when nanoporous goethite ore and oxygen were used; however, optimization of the reduction degree would likely improve it. Further investigations will be carried out to determine the optimum conditions for combustion synthesis to obtain a higher degree of reduction for this process.

**CONCLUSIONS**

In this study, carbon-infiltrated goethite ore was obtained by the tar impregnation method and it was partially reduced to metallic iron in an oxygen atmosphere regardless of extremely short time (less than 1 min) experiment. The conclusions of this study were as follows.

Tar impregnation and heat treatment of goethite ore produced carbon-infiltrated goethite ore with a thick carbon layer on its surface, and the presence of nanopores within the mildly calcined goethite ore resulted in nanocontacts between the iron ore and carbon.

Metallic iron was generated from the carbon-infiltrated goethite ore after rapid heating in an oxygen atmosphere. In contrast, metallic iron was not formed when nonporous materials (high-grade hematite ore, hematite reagent grain, or goethite ore calcined at over 1000 °C) were used; however, optimization of the reduction degree would likely improve it. Further investigations will be carried out to determine the optimum conditions for combustion synthesis to obtain a higher degree of reduction for this process.

**EXPERIMENTAL SECTION**

Three raw materials (goethite ore (Figure S1A), high-grade iron (hematite) ore, and Fe2O3 reagent) were used in this study. The goethite ore and high-grade iron ore contain 57 and 65 mass % of total Fe and 8.8 and 0.77 mass % of combined water (CW), respectively. The Fe2O3 reagent, which was used as a reference, had sizes of 2−5 mm and a purity of 99.5%.

Initially, all of the raw materials were crushed into 1−2 mm fragments and then calcined at 300 °C for 24 h in an air atmosphere to remove the CW (Figure S1B). Coal tar was used as the carbon source. The viscosity of tar itself is too high to infiltrate the pores of goethite ore. For this reason, toluene (C7H8, 99.5%) was added to the tar to reduce its viscosity. Tar and toluene were weighed at a mass ratio of 1:1 and then stirred at 50 °C to give a tar solution. A fraction of this tar solution (30 mL) was placed into an alumina crucible, and 10 g of the calcined iron ores was added. The iron ores with the tar solution were then heated at 500 °C for 1 h under an Ar flow. The obtained carbon-infiltrated ores were then crushed into 1−2 mm fragments (Figure S1C).

The CS experiments were conducted in a packed bed reactor. Carbon-infiltrated ores (100 mg) were placed into a quartz tube (ϕ 6 mm) and a thermocouple was placed under the ore, with the ore temperature controlled by a temperature controller. The ore was heated rapidly to the target temperature at a rate of 20 °C s⁻¹ and was maintained at that temperature for 10 s (Figure S1D). Gases were flowed from the top to the reactor at a constant gas flow rate of 1 L min⁻¹ (linear velocity: 0.6 m s⁻¹). The compositions of the flowed gases were 25 vol % O₂/Ar, Ar, or 20 vol % H₂/Ar. When O₂/Ar and H₂/Ar were flowed, the gas flow was immediately changed to Ar after the
Temperature changes of the samples during the CS experiments were measured every 200 ms by a thermocouple placed directly over the ore. Gas analysis was performed during the CS experiments every 1 s using gas chromatography–mass spectrometry (Thermostat D-35614 GSD 300 T3 Gas Analyzer Spectrometer, Pfeiffer Vacuum, Aslar, Germany). Phase identification and cross-sectional observation of the ore samples were conducted using X-ray diffractometry (XRD; Miniflex, Rigaku, Tokyo, Japan) and scanning electron microscopy (SEM; JSM-7001FA, JEOL, Tokyo, Japan) with energy dispersive X-ray spectroscopy (EDS). The nanostructures of the ore samples were observed using transmission electron microscopy (TEM; JEM-2010F, JEOL, Tokyo, Japan). The amount of carbon in the ore was determined using a CHN/O/S elemental analyzer (CE-440; EAI). The pore distribution, pore volume, and BET surface area were determined by N$_2$ adsorption–desorption measurements (Autosorb 6AG, Yuasa Ionics CO. Ltd., Osaka, Japan) at 77 K.

## ASSOCIATED CONTENT

1. Supporting Information

   The Supporting Information is available on charge of the ACS Publications website at DOI: 10.1021/acsomega.8b00958.

   Photographs of the ore samples in this study; cross-sectional EDS observations of the carbon-infiltrated goethite ore; and gas analysis during rapid heating of the carbon-infiltrated goethite ore in an inert atmosphere (PDF)

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Notes

The authors declare no competing financial interest.

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