Fabrication of Iron Particles from Porous CaO and Molten Iron Sulfide using Spontaneous Wettability Conversion

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Abstract
We propose a new method for fabricating iron particles from a porous CaO body and molten iron sulfide by spontaneous wettability conversion. We demonstrate the fabrication of iron particles via our proposed method. In the experiment, iron sulfide and a porous CaO body were reacted under a CO gas flow at 1823 K. Iron particles several micrometers in size were fabricated successfully using our method.

Key words
Fabrication, Iron Particle, Wettability, Porous CaO, Iron Sulfide

1. Introduction
Metal particles are used in a wide variety of materials for industrial applications. Many methods for producing metal particles have therefore been developed for the fabrication of desired metal particles [1–3]. There are three main methods for the production of metal particles: mechanical processes, chemical processes, and atomizing processes. Machining, milling, and mechanical alloying are included in mechanical processes, and can produce metal particles with a wide variety of sizes. Fine metal particles are chemically produced by reduction, precipitation, electrolysis, and decomposition of metal carbonyls. Atomizing processes such as gas atomization, water atomization, centrifugal atomization, and plasma rotating electrode processes have become mainstream techniques for producing metal particles for powder metallurgy, because of their high productivities. Metal particles are characterized based on their morphologies, and physical, chemical, and bulk properties. Recently, metal and alloy particles have been regarded as new functional materials, which not only support current technologies but also enable the creation of advanced technologies. It is therefore becoming important to discover new ways to produce metal and alloy particles with novel properties, because of the increasing demand for advanced materials; for example, the development of methods for producing phase-controlled metal particles is an important area. Conventional processes for producing metal particles cannot include thermal treatments, which control the metal particle phase, because of the problem of agglomeration of the produced metal particles.

Here, we propose a new method for fabricating iron particles by taking advantage of wetting properties, which can enable thermal treatment of particles. We demonstrate the fabrication of iron particles from a porous CaO body and iron sulfide via our proposed method.

Fig. 1 Principle of fabrication of iron particles from iron sulfide and porous CaO body using spontaneous wettability conversion

2. Principle of Fabrication of Iron Particles
The principle of the iron particle fabrication is shown in Fig. 1. The starting material and the medium for fabricating iron particles used in our process are iron sulfide and a porous CaO body, respectively. The porous CaO body consists of CaO particles. When molten iron sulfide is placed in contact with the porous CaO body, the molten iron sulfide penetrates the porous CaO body [Fig. 1(a) to (b)]. It has been reported that molten iron sulfide penetrates the interstices of oxides such as chromite and olivine, i.e., the wettability between the molten sulfide and oxides is good [4]. Based on this, we assumed that molten iron sulfide would penetrate an oxide with pores, such as a porous CaO body, because of good wetting. After penetration, the iron sulfide reacts with CaO to convert the molten iron sulfide to molten iron, and the surfaces of the CaO particles to CaS [Fig. 1(b) to (c)]. After the reaction, the molten iron tends to...
be located in the gaps between the CaS-coated CaO particles rather than at the particle boundaries [Fig. 1(c) to (d)]. The contact angle between CaS and molten iron, measured by Staronka et al. using the sessile drop method [5], was 87°, which is less than 90°, indicating slight wetting. In contrast, Nogi et al. [6] and Lee et al. [7] reported that the contact angle between CaO and molten Fe contains sulfur, measured using the same method, was slightly greater than 90°, which means slight non-wetting. In their studies, it was observed that a CaS layer was formed at the interface between CaO and the molten Fe due to the reaction of CaO and sulfur in molten Fe-S alloy. The measured angle was therefore the contact angle between CaS and molten iron. The contact angle between CaS and molten iron therefore remains controversial. In the present work, it was assumed that the wettability between CaS and molten iron would be poor, based on the results reported by Nogi et al. and Lee et al. The non-wetting condition results in a situation where molten iron is expelled from narrow spaces, i.e., the particle boundaries, to wide spaces, i.e., the gaps between the CaO particles, and some molten iron near the surface of the porous CaO body can exude from the porous CaO body [8]. Eventually, the molten iron present in the gaps forms iron particles [Fig. 1(d)]. The present method therefore produces iron particles from a porous CaO body and iron sulfide by spontaneous wettability conversion, based on the reaction between CaO and iron sulfide. In the present work, the fabrication of iron particles was attempted, based on this proposed principle.

3. Experimental

In the experiment, reagent CaCO$_3$ powder (3 g) was compacted using a cylindrical mold of diameter 20 mm under 1 MPa pressure. The compact was calcined and sintered at 1273 K for 10 h under an air atmosphere to form a porous CaO body. CaCO$_3$ releases CO$_2$ to form CaO above 1098 K. The cross-sectional image of the CaO body after calcining and sintering is shown in Fig. 2. It can be seen that the CaO body contains several micrometer-sized pores. Iron sulfide (0.02 g) and a piece of prepared porous CaO body (0.3 g) were used. A hole was created in the upper part of the porous CaO body and the iron sulfide was placed in the hole (Fig. 3). The sample, in a graphite crucible ($\phi 15 \times 11 \times 50$ mm), was kept under a CO gas flow [100 mL/min (stp)] at 1823 K. The reaction between iron sulfide and CaO is expressed by the following equation:

$$\text{FeS} + \text{CaO} + \text{CO} \rightarrow \text{Fe} + \text{CaS} + \text{CO}_2$$  \hspace{1cm} (1)

In addition, the experiment under Ar gas flow [100 mL/min (stp)] was conducted in order to confirm the state of penetration of molten iron sulfide before reaction (1) occurs, i.e. the state of Fig. 1(b). The selected temperature is above the melting points of iron sulfide (1467 K) and metallic iron (1811 K); i.e., both iron sulfide and iron were in the liquid state at the experimental temperature, 1823 K. After a holding time of 1 h for CO or 10 min for Ar, the sample was cooled by Ar gas blowing. The sample was mounted on epoxy resin. The mounted sample was cut to create a cross section, and the cross section was polished. The cross section was examined using scanning electron microscopy (SEM).

4. Results and Discussion

Figure 4 shows the sample appearance after the experiment with a CO gas. There are reacted (grey) and unreacted CaO (white) areas. The reacted area spreads from the hole in the CaO body. It is suggested that molten iron sulfide penetrated the porous CaO body, as expected. The cross-sectional view obtained using SEM is shown in Fig. 5. The figure also shows area analysis of the elemental distribution, obtained using energy-dispersive X-ray spectroscopy (EDX). The target elements are calcium, iron, oxygen, and sulfur. It can be seen that iron does not exist at the pore boundaries but is present as individual particles of sizes several micrometers in the pores, as expected. In contrast, oxygen and sulfur are distributed almost homogeneously. It is difficult to confirm the presence of CaS and CaO.

The content of sulfur impurities in the iron particles produced by our method is of interest. In their studies, Nogi et al. [6] and Lee et al. [7] concluded that molten iron contains some sulfur, because the surface tension of the produced molten iron was much lower than that of pure iron. However, Tanaka et al. [9] showed that the use of small capillary tubes in porous CaO effectively desulfurizes the molten iron. Although a large amount of sulfur is present in our method, because of the use of iron sulfide as the starting material, the penetration by molten iron sulfide may effectively decrease the sulfur content. The analysis of sulfur content for cross-sectional surface of iron particle was conducted by EDX although the precision obtainable is limited. The measured sulfur content of iron particle obtained in the present experimental condition was...
0.2 mass%. However, it is necessary to conduct the analysis by a high accurate method like infrared absorption method to determine the sulfur content precisely.

![SEM image](image1.png)

**Fig. 5** Cross-sectional image of sample under a CO gas and area analysis of elemental distribution

![SEM image](image2.png)

**Fig. 6** Cross-sectional image of sample under Ar gas

Figure 6 shows the cross-sectional view of sample under a CO gas atmosphere. In contrast to the sample under a CO gas, a substance exists at the pore boundaries. The substance at the pore boundaries was confirmed to be iron sulfide by EDX analysis and the other was CaO. This indicate that the molten iron sulfide penetrate the porous CaO body by the good wettability between CaO and iron sulfide. In addition, it is concluded that the formation of iron particles occurs after the reaction (1), and is attributed to the wettability conversion, *i.e.* wetting to non-wetting, associated with the reaction. This is because that molten iron is not expelled and still located at the particle boundaries due to capillary effect in case that the wettability between CaS and molten Fe.

![Diagram](image3.png)

**Fig. 7** Magnetic separation system, separated substance, and residue

We tried to collect iron particles selectively from the sample using magnetic separation. The setup for magnetic separation is shown in Fig. 7. The unreacted CaO was roughly removed from the sample. The remaining reacted part was crushed and ground in a mortar. The ground sample was placed in acetone in a beaker. The substance, which was attracted by a magnet, was collected using a magnet placed beside the beaker, while stirring the acetone. The constituent phases of the magnetically collected substance and residue were confirmed using X-ray diffraction (XRD). The XRD patterns are shown in Fig. 8. It is found that both substances consist of iron, CaS, CaCO$_3$, and Ca(OH)$_2$, and the iron is present as α-iron. It is expected that Ca(OH)$_2$ was formed by reaction of CaO in the sample with moisture in the air or water in the acetone during crushing, grinding, and magnetic separation. The presence of CaCO$_3$ can be explained by the reaction of Ca(OH)$_2$ with CO$_2$ in air. The iron peak in the magnetically collected substance is stronger than that in the residue, using the peaks of the other constituents, *i.e.*, CaS, CaCO$_3$, and Ca(OH)$_2$, as the bases. This means that the magnetically collected substance contains more iron particles than the residue does, although we did not achieve perfect selective collection of iron particles. Therefore, the sulfur content of the iron particles produced in the present work could not be accurately determined by infrared absorption method, because separation of the iron particles was unsuccessful.

SEM images of the magnetically separated substances are shown in Fig. 9. This confirmed the presence of iron particles several micrometers in size, as in the cross-sectional observation in Fig. 4. In addition to iron particles, many other substances such as CaS are observed, as expected from the XRD results, and the sizes of the substances range from 1 to 20 μm in the observation. The iron particles and those of other substances were distinguished using EDX. From the above results, it is concluded that our proposed method can produce iron particles in a porous CaO body.
In principle, our proposed method as described in Fig. 1 can be used for elements other than iron, and even alloys, if the conditions for wetting conversion and the contact angles are satisfied. In terms of the penetration of molten sulfides into porous oxides, it is expected that pure copper sulfide and iron sulfide containing nickel, copper, or cobalt would satisfy these conditions [4, 10]. However, there is a lack of data on wettabilities between CaS and molten metals or alloys. Furthermore, in principle, the metal particle size can be controlled by varying the pore size of the porous CaO body. Moreover, particles made using our method do not agglomerate, even at high temperatures, because the particles can be kept in the gaps in the porous body, as shown in Figs. 1 and 5. In general, the metal particles produced using conventional methods such as gas atomization cannot be treated using thermal processes, which cause phase transitions and changes, due to the problem of agglomeration of the metal particles. It is therefore difficult to produce metal particles with a desired phase by thermal treatment. In contrast, in situations where the particles exist independently, as in the present method, metals with specific phases can be produced by thermal treatment. This can lead to metal particles with novel properties. In either case, however, the separation of the metal particles from the porous body is a critical issue, which needs to be overcome.

5. Conclusions
A new method for fabricating iron particles based on spontaneous wettability conversion, involving reaction of a molten iron sulfide with a porous CaO body is described. Iron particles were fabricated using our proposed method, and iron particles of size several micrometers were obtained under the described experimental conditions.

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References