Mechanisms of Pig-iron Making from Magnetite Ore Pellets Containing Coal at Low Temperature

Kazuhiro NAGATA, Rie KOJIMA, Taichi MURAKAMI, Masahiro SUSA and Hiroyuki FUKUYAMA

Department of Chemistry and Materials Science, 1) Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552 Japan.

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A new pig-iron making process using magnetite ore pellets containing coal as reducing agent has been investigated. The pellets were heated rapidly in argon at furnace temperatures between 1 573 and 1 723 K and the temperature and partial pressure of oxygen in the pellets were recorded in situ. Molten iron containing 1.1–3.6 mass% carbon over the composition on the liquidus line of iron–carbon system was produced at the furnace temperatures higher than 1 598 K within 16 min. The whole process consists of four steps, i.e., heating, reduction of iron ore, carburization and melting of pig iron. The solution-loss of carbon and the reduction of iron ore are coupled and concentrically take place from the surface to centre due to the heat transfer control because of the endothermic reaction of solution-loss. The reduced iron particles were carburised by CO gas, rapidly absorbed carbon from coal and become molten pig iron particles. The particles cohered to make large drops and the pellet suddenly collapsed to melt. The conditions determining the lowest temperature for producing pig iron are discussed.

KEY WORDS: pellet; coal; magnetite ore; pig iron; reaction mechanisms.

1. Introduction

Currently, steelmakers are facing the situation that they must urgently establish new pig iron and steelmaking processes due to the shortage of suitable energy resources and the introduction of more stringent environmental laws. One solution of this problem is to develop a new process for producing molten pig iron in shorter time and at lower temperature than blast furnace methods.

FASTMET process is one of such processes in which iron oxide pellets containing coal are heated rapidly and thereby 96–98% of metallisation can be attained within 900 s at temperatures between 1 473 and 1 573 K. This process uses turn-table-type hearth heated by radiation and the pellets are charged on the hearth in mono layer. In addition, it has been reported that after the reaction carbon still remains in the centre of produced iron and would allow molten iron to be produced. The process is called as ITmk3 and the pilot plant was operated 3 times at 1 623 K for 100 h during 6 months from October 1999.

Such a low temperature operation producing molten pig iron has been established in “Tatara” furnace. The “Tatara” is a Japanese traditional process for making mainly molten pig iron with steel bloom from iron sand and charcoal in a box type furnace with 1.2 m heights. The “Tatara” had been commercially operated until 1922. The productivity of molten pig iron and steel bloom depends on the carbon content in reduced iron in equilibrium with liquid according to the iron–carbon system. The carbon in reduced iron is absorbed above the tuyer of the “Tatara” furnace. The reaction mechanisms of “Tatara” are resembled to that of FASTMET.

However, Matsumura et al. have not clearly determined the lower limit of temperature for producing molten pig iron and have not analysed the mechanisms relevant to the whole process in detail, although these are very important to realise pig iron making at lower temperature. Consequently, the aims of this study are to investigate reduction and melting mechanisms of pellets of iron oxides containing coal when heated up rapidly, and to suggest a possibility of pig iron making at lower temperature.

2. Experimental

2.1. Sample Preparation

Spherical green pellets (ca. 10–25 mm diameter) of magnetite ore, named Romeral, containing coal were prepared using a pelletiser from iron ore (ca. 50 μm diameter), coal (ca. 40 μm diameter) and bentonite powders, the last serving as a binder. Two kinds of coal of A-type and B-type were used, which correspond to Pellet A and Pellet B, respectively. Chemical compositions of the raw materials are given in Table 1. These powders were mixed with 2 mass% of binder. The amount of coal was determined by taking into account the amount of carbon required for reducing iron ore completely and forming CO gas as well as that required for carburizing so as to obtain iron containing 2 mass% of carbon. The apparent density of pellets is 2.11 to 2.32 g·cm⁻³.
2.2. Observation of Pellets during Reaction

Figure 1 shows the reaction furnace of pellets to investigate the lowest temperature for producing molten pig iron. The inner diameter of the reaction tube was 60 mm. Two MgO crucibles were placed in the tube: the upper (50 mm outer and 38 mm inner diameters and 150 mm height) was for reducing pellets and melting produced iron by carburisation and had 17 holes (6 mm diameter) drilled at the bottom to filtrate molten pig iron, and the lower (50 mm height) was for collecting the products. After placing the crucibles in the uniform temperature zone of the furnace, argon gas was supplied into the reaction tube at the flow rate of 100 Nm$^3$/min. Confirming that the furnace temperature was controlled to the desired temperature, several pellets were dropped one by one into the upper crucible from the top of the furnace. The temperature of the reaction site was monitored using a R-type thermocouple near the pellet during the reaction, as shown in Fig. 1. In addition, the appearance of the pellet was observed with the naked eye through the view port at the top of the reaction tube. The furnace temperature was controlled from 1573 to 1723 K, which led to determining the lowest temperature at which molten pig iron was produced. Iron samples collected in the lower crucible were used to analyse carbon concentration by the Orsat method and the other compositions by EDAX.

2.3. Measurements of Oxygen Partial Pressure and Temperature in Pellets

To investigate reduction and melting mechanisms, three kinds of experiments were carried out: (1) measurements of temperature, total pressure and oxygen partial pressure in the centre of pellets, (2) observations of the cross section of pellets in reaction and (3) measurements of carbon distribution in produced iron in pellets.

Figure 2 shows the experimental setup to measure temperatures and oxygen partial pressures in the centre and surface of pellet simultaneously throughout the reaction process. R-type thermocouples and needle-type oxygen sensors (3.5 mm diameter and 33 mm length) were installed in the centre and surface of pellet and the gap between the pellet and the sensor in the centre was sealed with alumina cement near the pellet surface. The oxygen sensor of Galvanic cell was composed of the one-end closed tube of ZrO$_2$, 8mol%MgO electrolyte, on the top of which Pt wire (0.3 mm diameter) was wound as an electrode. Cr(s)/Cr$_2$O$_3$(s) powder mixture was stamped in the tube as a reference electrode with Mo or Pt lead wire, which fixed the equilibrium partial pressure of oxygen. The pellet was held in an alumina crucible (40 mm outer and 35 mm inner diameters and 70 mm height) and the crucible was rapidly got down in the uniform temperature zone of reaction tube (42 mm inner diameter) under argon gas flow (200 Nm$^3$/min).

From the electromotive force of oxygen sensor, the partial pressure of oxygen, $P_{O_2}$, was determined using the following equation:

$$E = (RT/4F) \ln[P_{O_2}/P_{O_2}(\text{ref})]$$

$P_{O_2}(\text{ref})$ is the partial pressure of oxygen of the reference electrode in equilibrium with Cr and Cr$_2$O$_3$ and calculated from the standard Gibbs energy of formation for Cr$_2$O$_3$.$^{61} R$ is the Gas constant, $F$ the Faraday constant and $T$ the absolute temperature. The thermoelectric power between Mo and Pt wires was corrected based upon data obtained in the preliminary experiment.

2.4. Measurement of Total Pressure in Pellet

The total pressure in the centre of pellet was measured by

Table 1. Chemical composition of raw materials (mass%)

|        | T. Fe | FeO | S | SiO$_2$ | Al$_2$O$_3$ | CaO | MnO |
|--------|-------|-----|---|---------|-------------|-----|-----|
| Iron ore | 69.51 | 30.22 | 0.02 | 1.42 | 0.41 | 0.46 | 0.40 |
| Binder | 2.60 | — | — | 69.20 | 14.60 | 0.94 | 1.76 |

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a semiconductor pressure gauge that was connected to one end of a silica tube installed in a pellet instead of the oxygen sensor. The inside and outside diameters of silica tube was 2.5 and 3.5 mm, respectively.

2.5. Observations of Cross Section of Pellets and Carbon Distribution in Reduced Iron

A pellet only with a thermocouple in the centre held in an alumina crucible was got down and kept in the resistance furnace at 1623 K for 150–510 s under argon gas flow. After then the alumina crucible was taken out from the furnace and quenched into water. The pellet was cut and the cross section of pellet was mechanically polished. The cross section was observed and the carbon distribution was measured by electron probe microanalysis (EPMA).

3. Results

3.1. Change in Appearance of Pellets

Shortly after a pellet was dropped into the upper crucible at 1673 K, soot was produced from the pellet, which did not allow the pellet to be observed. About 90 s later, the soot disappeared and cracks were observed on the surface of the pellet. About 450 s later, the surface of pellet melted and many fine particles of metal oxides such as silica and alumina splashed from the surface. Then, the pellet began to lose its shape and some liquid flowed down into the lower crucible. About 610 s later, the pellet was completely broken and many fine particles were left in the upper crucible. Several iron droplets were collected in the lower crucible, as shown in Fig. 3, which was produced from 5 pellets. Some slag particles are appeared on the surface of iron droplets and not in the droplets. The same reaction behavior of pellets was observed in the experiments at furnace temperatures higher than 1598 K.

Just after dropping a pellet into the crucible at 1673 K, temperature near the pellet suddenly decreased by almost 100 K and arrived at a minimum after about 50 s, as shown in Fig. 4(a). Then it gradually increased and recovered at the furnace temperature after about 600 s.

As shown in Fig. 4(b), the time for pellet to melt became shorter as the furnace temperature increased. The lowest temperature to produce molten iron in this process was 1623 K for the pellet including A-type coal with 20 mm diameter, 1638 K for the pellet with 15 mm diameter and 1723 K for the pellet with 10 mm diameter. On the other hand, the pellet including B-type coal with 20 mm diameter melted at the lowest temperature of 1598 K.

The carbon concentration in molten pig iron produced at various furnace temperatures is 1.06 to 3.60 mass% and tends to decrease with increasing furnace temperature, as shown in Fig. 5. The carbon concentration is near or over the liquidus composition of the iron–carbon system.

![Fig. 3. Pig iron dropped in the lower crucible after experiment using 5 pellets at 1673 K.](image)

![Fig. 4. (a) Temperature change near pellet and (b) time at melting start and lowest temperature for melting.](image)
3.2. Total Pressure, Temperature and Partial Pressure of Oxygen in Pellets

The changes of total pressure and temperature in the center of a pellet were measured at the furnace temperature of 1673 K. At the beginning of the measurement, the total pressure increased rapidly and attained to about 1.3 atm at about 60 s due to volatilisation of H₂, CO, CH₄ and so on contained in coal and expansion of gas. Then it decreased and settled down to about 1 atm.

Figure 6 shows the changes of temperature and partial pressures of oxygen at the center and surface of pellets with different diameters at the furnace temperature of 1673 K. The calculated $P_{O_2}$ is equilibrated with C(s) and CO(g) (1 atm).

3.3. Cross-section and Carbon Distribution in Reduced Iron in Pellets

Figures 8 shows the cross-sectional views of pellets, where (a) and (b) are in stage II, (c) at the turning point from stage II to stage III, (d) and (e) in stage III, (f) at the end of stage III and (g) at the beginning of stage IV. Inspection of these figures indicates that the layer of reduced iron is concentrically formed from surface to centre of pellet and that the reduction reaction of iron ore finishes by the end of stage II. This means that heat transfer determines the reduction rate across pellet. In the figure (f) the pellet shrinks and separates into two parts, outer shell and inner iron.
inner core, and then suddenly loses its shape as shown in the figure (g).

Figure 9 shows the distribution of carbon concentration in reduced iron (a) in pellet at the end of stage II and (b) in the core at the end of stage III, respectively. At the end of stage II, the carbon content in reduced iron is 0.25 to 0.35 mass% near the surface of pellet and 0.15 mass% at the centre. The reduced iron is carburized from surface to centre of pellet following the reduction in stage II. At the end of stage III, the carbon content is 1.6 to 2.0 mass% near the surface of inner core and 1.36 mass% at the centre, which is in the mixture phase of solid and liquid in the iron–carbon system at 1 623 K. In Fig. 9(a), the carbon content in reduced iron decreases near the surface of pellet.

3.4. Impurities in Produced Pig Iron

Figure 10 shows the concentration of impurities in pig irons produced at 1 623, 1 673 and 1 723 K. The concentration was measured by chemical analysis. The content of silicon increases from 0.4 to 0.8 mass% with decreasing temperature and those of calcium and manganese are almost constant to be about 0.2 mass%. The contents of phosphor and sulphur are less than 0.1 mass% and decrease with decreasing temperature. Especially these elements are trace at 1 623 K. Because silicon and oxygen was detected the same area by means of EPMA, it is clear that these elements exist as silica of about 15 μm in the mean diameter.

4. Discussion

4.1. Reduction Mechanisms of Iron Ore in Pellet Containing Coal

The reduction reactions of iron ore are expressed as

\[
\text{Fe}_3\text{O}_4 (s) + \text{CO} (g) \rightarrow 3\text{FeO} (s) + \text{CO}_2 (g) \quad \text{(1)}
\]

\[
\text{FeO} (s) + \text{CO} (g) \rightarrow \text{Fe} (s) + \text{CO}_2 (g) \quad \text{(2)}
\]

and these reactions are coupled with the solution-loss reac-
tion of carbon;

\[ \text{C (s)} + \text{CO}_2 (g) \rightarrow 2\text{CO (g)} \quad \text{(3)} \]

The partial pressures of CO (g) and CO\(_2\) (g) are determined from the oxygen partial pressure measured by an oxygen sensor under the total pressure of 1 atm. At the beginning of stage II, oxygen partial pressure on the surface of pellet with 22 mm diameter is \(1 \times 10^{-12}\) atm at 1 520 K. Thus, the ratio of partial pressures of CO\(_2\) to CO is calculated to be 0.16. In the end of stage II, the oxygen partial pressure and the ratio on the surface decrease to \(1 \times 10^{-14}\) atm and 0.002 respectively at 1 673 K, and at the center near to \(2 \times 10^{-15}\) atm and 0.003 respectively at 1 580 K. These conditions make the chemical affinities of reactions (1) to (3) positive. It means that the solution-loss of carbon and the reduction of iron ore by CO (g) proceed simultaneously.

Matsumura et al.\(^3\) used a pellet with the diameter of 17 mm and found the ratio of CO/(CO\(_1\)CO\(_2\)) in out gas decreasing during reducing a pellet. They reasoned that the reaction rate of solution-loss is slower than that of the reduction of iron oxide under lower temperature.

After the evaporation of volatile gases in coal in stage I, the reactions start at the surface of pellet and the rate of reactions attains at a maximum with the highest ratio of CO\(_2\)/CO at the end of stage I. During the stage II, the product layer of iron shell becomes thicker in process of reactions. CO\(_2\) gas formed by the reduction of iron ore diffuses to the surface through the layer and gasifies residual carbon in the layer to produce CO gas. Thus, the carbon content in reduced iron near the surface decreased, as shown in Fig. 9(a).

Because the solution-loss reaction is endothermic, the heat flowing from the surface is partly absorbed at the concentric reaction site. Then, the temperature rise in the centre of pellet is suppressed and the plateau of temperature appears in the stage II. The reactions scarcely take place inside of the reaction site and the oxygen partial pressure in the centre gradually increases with temperature rise.

At the end of stage II, the reactions of reduction and solution-loss in a pellet cease after attaining the highest ratio of CO\(_2\)/CO in its center.

4.2. Carburization and Melting Mechanisms

In the stage III of Fig. 6, the partial pressure of oxygen in the centre of pellet gradually decreases to near that in equilibrium with carbon and CO gas of 1 atm and the carburization of reduced iron by coal proceeds.\(^3\) In Fig. 11, the relation between oxygen partial pressure and temperature in the centre of pellet are drawn on the phase diagram of iron–carbon–oxygen system. The maximum partial pressure of oxygen corresponds to the minimum carbon activity in \(\gamma\)-Fe. The reduced iron, however, rapidly absorbs carbon from coal rather than CO gas\(^9\) because there is the difference of carbon content between solid and liquid by about 1 mass% in equilibrium at 1 623 K. Then, carbon activity increases and enters into liquid phase at the end of stage III. The higher furnace temperature gives the lower carbon activity at the maximum partial pressure of oxygen and results the higher temperature for melting. These results means that the carbon content of pig iron in a pellet depends on that of reduced iron particles carburised by CO gas in stage II, that is, the higher carbon content of reduced iron has at the end of stage II, the higher carbon content of pig iron attains.

From Figs. 8(d) and 8(e) in stage III, it is observed that the outer shell of pellet becomes porous and partially melts, respectively. The carbon content in reduced iron has not saturated at the end of stage II, as shown in Fig. 9(a). Though a pellet still keeps the round shape at the end of stage III, the core of pellet is composed of the mixture of solid and liquid pig iron particles, as shown in Fig. 9(b). Liquid pig iron particles in the outer sell have already cohered to be big droplets and dropped down. Then, the molten pig iron in the outer shell contacts with residual iron in the inner core and accelerates the carburization and melting.

The pellet without melting has the almost same view of cross-section as that shown in Fig. 8(d). The result of No. 3 (\(\odot\)) in Fig. 7 shows that the oxygen partial pressure in the centre of pellet without melting at 1 573 K also decreases slowly in stage III and gradually increases to the oxygen partial pressure in equilibrium with C and CO (g) of 1 atm in stage IV. The concentration of carbon in iron particles in the outer shell of pellet is in the coexistence phase of solid
and liquid near solidus line, as shown in Fig. 5, which is too low to cohere to be large droplets.

4.3. Size Effects on the Lowest Temperature for Production of Molten Pig Iron

A small pellet is more rapidly heated than large one and the periods of stage I and II are shorter, while the period of stage III is almost same as large one, as shown in Fig. 6. The reason is that the carburization is not controlled by heat supplied from the surface. The reduction of iron ore in a small pellet more rapidly proceeds to produce CO2 gas in stage II and the partial pressure of CO2 in a small pellet becomes higher than that in a large one. Then, the maximum partial pressure of oxygen in the center of a small pellet is higher than that in large one, as shown in Figs. 6 and 11. Under the higher partial pressure of oxygen and the shorter reaction time, the activity and content of carbon in reduced iron are lower at the end of stage II and the carbon content of pig iron becomes lower. Thus, the melting temperature of a pellet is elevated.

4.4. Roles of Slag for Carburizing and Melting of Pellet

As shown in the EPMA analysis of Fig. 12, a pellet without melting at 1 673 K had many small iron particles partially in solid and liquid mixture in the outer shell of pellet and the iron particles were surrounded by FeO-rich silicate slag (fayalite). From the observation of pellet after about 450 s, at the end of stage III, the surface of pellet melted and many fine particles of metal oxides splashed from the surface. This means that fayalite melt is produced in this stage. Fayalite melt is in equilibrium with solid iron under oxygen partial pressure of about 10−12 atm at 1 450 K. This melt is easy to wet with iron because of bigger surface tension of molten pig iron than the interface tension of iron and molten fayalite. Thus, the melt tends to cohere pig iron particles.

The pellet containing B-type coal decreases the temperature for producing molten pig iron to 1 598 K, as shown in Fig. 4(b). The B-type coal has higher content of ash and lower content of Al2O3 in ash than A-type coal. The slag in B-type coal seems to be formed more and to melt at lower temperature than that in A-type coal.

Therefore, molten slag plays an important role in cohering particles of molten pig iron to make large drops.

4.5. Conditions Determining the Lowest Temperature for Making Pig Iron

Matsumura et al. determined the lowest temperature for making pig iron from a pellet containing coal with the diameter of 17 mm to be 1 653 K. Their results are in good agreement with the present results. They increased the content of coal in a pellet more than 21.5 mass% and found the pellet melting to be molten pig iron. However, more content of coal in a pellet did not decrease the lowest temperature for making pig iron. The reason is that the carbon matrix in a pellet prevents pig iron particles from cohering. As mentioned above, FeO-rich silicate slag plays a role in cohering the particles.

From the above discussions, the conditions determining the lowest temperature are 1) higher carbon content of reduced iron particles in a pellet carburized by CO gas in stage II, 2) optimum coal content in a pellet and 3) optimum ash content in coal.

4.6. Behaviour of Impurities in Molten Pig Iron

It was analysed by EPMA that Silicon, calcium and Manganese in pig iron exist as their oxides. Phosphor and sulphur dissolved in pig iron at 1 623 K are less than 0.01 mass%. For the Tatara operations, silicon content in pig iron is trace and phosphor and sulphur contents are 0.03 and 0.01 mass%, respectively, though charcoal has been used as fuel instead of coal. The equilibrated content of silicon with silica is thermodynamically calculated to be 0.45 mass% under the oxygen partial pressure of 1×10−15 atm and 2.60 mass% under that of 1×10−16 atm at 1 623 K. The partial pressure of phosphor equilibrated with 4CaO·P2O5, 3CaO·P2O5 and SiO2 is 1.7×10−3 atm under the oxygen partial pressure of 1×10−15 atm and 0.53 atm under that of 1×10−16 atm at 1 623 K. These high phosphor partial pressures mean that almost phosphor in iron ore and coal dissolves into molten pig iron. The reasons why the contents of impurities in pig iron are very low are the high production rate of molten pig iron and the rapid separation of pig iron from molten slag by a filter. In other words, the time for contacting molten pig iron and slag is short.

5. Conclusions

Magnetite ore pellets containing coal as reducing agent were heated rapidly in argon at furnace temperatures between 1 573 and 1 723 K, and molten iron containing 1.06 to 3.60 mass% of carbon was produced at the furnace temperatures higher than 1 598 K within about 16 min. The primary factors of producing pig iron at lower temperature are 1) higher carbon content of reduced iron particles in a pellet carburised by CO gas in stage II, 2) optimum coal content in a pellet and 3) optimum ash content in coal.

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