Behaviour of New Zealand ironsand during iron ore sintering

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Abstract
Titanium-bearing burdens are commonly introduced into blast furnaces to protect the hearth because the so-called "titanium bear" which is a precipitate of carbide, nitride and carbonitride of titanium may form in the blast furnace hearth if TiO2 is present in the feed [1, 2]. New Zealand ironsand is a titanomagnetite, containing around 60 wt.% iron, 8 wt.% titanium and other substances such as silica, phosphorus and lime [3, 4]. Since it is competitive in price, introduction of the ironsand into the ferrous feed can reduce the production cost and potentially increase blast furnace campaign life. An appropriate method of introduction of ironsand is as a component of the sinter as the small size of ironsand precludes direct charging into the blast furnace. Although the effect of introducing titanomagnetite into iron ore blends has been investigated [1, 2, §], little is known about the detailed sintering mechanism. The present study is aimed at identifying the sintering behaviour of New Zealand ironsand as well as the interaction between New Zealand ironsand and CaO to gain better understanding of sintering mechanism of titanomagnetite.

Keywords
iron, behaviour, ore, sintering, during, ironsand, zealand

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Behaviour of New Zealand Ironsand during Iron Ore Sintering

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Keywords: New Zealand ironsand; titanomagnetite; sintering; iron ore

Titanium-bearing burdens are commonly introduced into blast furnaces to protect the hearth because the so-called "titanium bear" which is a precipitate of carbide, nitride and carbonitride of titanium may form in the blast furnace hearth if TiO₂ is present in the feed [1, 2]. New Zealand ironsand is a titanomagnetite, containing around 60 wt.% iron, 8 wt.% titanium and other substances such as silica, phosphorus and lime [3, 4]. Since it is competitive in price, introduction of the ironsand into the ferrous feed can reduce the production cost and potentially increase blast furnace campaign life. An appropriate method of introduction of ironsand is as a component of the sinter as the small size of ironsand precludes direct charging into the blast furnace.

Although the effect of introducing titanomagnetite into iron ore blends has been investigated [1, 5, 6], little is known about the detailed sintering mechanism. The present study is aimed at identifying the sintering behaviour of New Zealand ironsand as well as the interaction between New Zealand ironsand and CaO to gain better understanding of sintering mechanism of titanomagnetite.

Experimental Procedure
The raw materials for this study were iron ore blend, limestone, silica sand, manganese ore and Cold Return Fines (CRF). Each was crushed and screened to a particle size smaller than 200 μm before use. These materials were proportioned according to BlueScope Steel’s Sinter Plant practice. To investigate the effect of ironsand concentration, 0 wt%, 3 wt% and 5 wt% ironsand were introduced into the mixture of which 1.0 g was then pressed into cylindrical tablets (8 mm diameter, ~5 mm height. The samples were sintered in a vertical tube furnace at three different temperatures (1100°C, 1200°C, and 1300°C) in a gas mixture of CO = 1%, CO₂ = 24%, and Ar = 75% (previous work by Hsieh and Whiteman [7] had shown the gas mixture simulated industrial sintering). After sintering for the desired time, the samples were directly removed to the cool top end of the reaction tube. Then the samples were mounted in epoxy resin and cut parallel to the original top surface of the sample, and polished in preparation for optical and scanning electron microscopy (SEM).

To study the microstructural development greater detail, interaction couples were prepared for ironsand and CaO powder and heat treated under Argon at 1100, 1200, and 1300°C as before. After sintering, the pellets were sectioned perpendicular to the interface and polished. The compositions of the phases in the cross sections were analysed by SEM/EDS.
Results

Assimilation of New Zealand ironsand into melts during sintering

The extent of coalescence of particles in raw mixture increased gradually with an increase in sintering temperature and time. At 1100°C, the assimilation effect was not remarkable. The amount of silicate bonding phase became pronounced at 1200°C. At 1300°C, the agglomeration of oxide materials was near complete and domains were dominated by polycrystalline masses of magnetite distributed in continuous silicate matrix. Titanomagnetite grains remained identifiable in the samples sintered at 1100°C and 1200°C and the hematite exsolution lamellae coarsened marginally with time. In a sample sintered at 1300°C for 12 minutes, very limited evidence of relict titanomagnetite grains suggests a large proportion of the ironsand had assimilated into the sintered mass.

EDS results showed the reactions started with lime in contact with acidic oxide compounds in the mixture. Therefore, calcium silicate phase containing iron oxides and alumina formed. As temperature and time increased, the new phase (with melting point of 1200°C) gradually melted and seeped between the large grains of the mixture including ironsand grains, dissolving these grains progressively. As the surface of titanomagnetite dissolved into the melt, a reaction zone around a ironsand grain was established, gradually increasing with time. In this zone, Ca$^{2+}$ from silicate melt diffused into the Fe$_3$O$_4$ lattice, with Fe$^{2+}$ diffusing in the opposite direction towards the melt. On one hand, the diffusion of Ca$^{2+}$ to Fe$_3$O$_4$ decreased the melting point of Fe$_3$O$_4$ and accelerated the melting rate of titanomagnetite grain. On the other hand, CaO$\cdot$TiO$_2$ was generated as the result of the reaction between TiO$_2$ and CaO.

Figure 1. EDS line analysis across the reaction zone of a New Zealand sand and CaO couple heated at 1200°C for 20 minutes

Figure 2. EDS line analysis across the reaction zone of a New Zealand sand and CaO couple heated at 1300°C for 12 minutes

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Interaction between New Zealand ironsand and CaO

A reaction zone between the ironsand and CaO layers was formed in the sample heated at 1200°C that became wider with increasing heating time and temperature. Figure 1 shows the elemental distribution across the reaction zone of a sample heated at 1200°C for 20 minutes. Ca$^{2+}$ from CaO diffused into the lattice of Fe$_3$O$_4$, and Fe$^{2+}$ diffused in the opposite direction into CaO. As a result, the reaction zone contained a high and uniform level of Ca and a relatively low level of Fe. The reaction zone consisted of two subzones, one being next to the unreacted ironsand layer with a relatively high TiO$_2$ concentration (notably higher than the average for an ironland particle), while the other close to the CaO layer having a high level of iron oxides. In the sample heated at 1300°C for 12 minutes (Figure 2), the subzone containing more iron oxides melted and penetrated into the CaO layer due to formation of a large amount of calcium ferrite (with low melting point), while the TiO$_2$-rich subzone became wider and did not melt since TiO$_2$ increases the liquidus temperature of CaO-TiO$_2$-FeOx system.

References