Silico-ferrites of calcium and aluminium (SFCA) are desirable phases in a high quality iron ore sinter product. The effects of sintering temperature, CaO/SiO₂ ratio, sintering gas atmosphere and cooling procedure on the phase composition of sintered specimens from an industrial sinter blend were examined with focus on the formation of SFCA phases. The proportions of mineral phases in specimens sintered at 1250–1325°C were quantitatively examined using image analysis. SFCA can be formed at low temperatures by solid state reactions, the formation of which was enhanced by increasing temperature. Further increasing sintering temperature promoted the reduction of Fe³⁺ in the SFCA crystal structure to Fe²⁺ and consequent decomposition of SFCA. At high temperatures, SFCA was produced during cooling via crystallisation from a silicate melt. Maintaining a high oxygen partial pressure favours the formation of SFCA, either via solid state reactions or from a melt. This is attributed to hematite being available as a reactant for SFCA formation. Similarly, increasing CaO/SiO₂ ratio provides more CaO as a reactant and promotes SFCA formation.

KEY WORDS: sintering; iron ore; silico-ferrites of calcium and aluminium; phase composition.

1. Introduction

In industrial iron ore sintering, the combustion of coke breeze supplies the necessary heat to achieve partial melting of raw materials. It also produces a locally reducing atmosphere within the sinter bed during the heating stage. Once the peak temperature has been reached, the agglomerated semi-molten material then slowly cools under an atmosphere with higher partial pressure of oxygen. The final sinter predominantly consists of primary and secondary hematite, magnetite, complex calcium-rich ferrite (s) and glassy silicate phases. Their relative proportion depends on the sintering conditions, such as temperature, raw sinter mix composition, oxygen partial pressure, basicity (CaO/SiO₂ mass ratio) and sintering time, which are controlled by operating parameters such as sinter blend composition, coke breeze rate, humidity, windbox pressure, and bed height.

Some attempts have been made to study how various mineral phases, particularly the complex calcium ferrites, are developed during the sintering process. Sasaki and Hida discussed the reactions in sintering process and concluded that complex calcium ferrites such as SFCA-I, an Fe-rich phase of silico-ferrite of calcium and aluminium with a characteristic acicular texture, are present in iron ore sinter if the temperature remained below 1300°C. If however, the temperature of sintering exceeded 1300°C, the early formed SFCA-I would breakdown to a calcium silicate melt and either Fe₃O₄ at low oxygen partial pressure (pO₂) or Fe₂O₃ at high pO₂. Upon cooling, Sasaki and Hida observed that a different complex calcium ferrite (now termed SFCA), crystallised. This was distinguished from SFCA-I by its coarse-grained columnar crystal morphology, and its lower Fe and higher Si content.

To examine the effect of oxygen partial pressure on sinter phase formation, Hsieh and Whiteman conducted experiments in which small tablet specimens made from powdered materials were rapidly heated in a tube furnace under controlled gas atmospheres to a temperature in the range 1180–1255°C. They found that a medium pO₂ value of 5×10⁻³ atm maximised the formation of complex calcium ferrites in the heating stage. In the cooling stage, magnetite could be oxidised to hematite and also react with the silicate melt to produce a large amount of columnar calcium ferrite (SFCA).

Wang et al. terminated the sintering process during pot tests and analysed specimens taken in different layers by optical microscopy and scanning electron microscopy.
including 5 wt% ironsand are examined with focus on the formation of SFCA phases. The laboratory scale study employing systematic variations in operating parameters permits a detailed analysis of the microstructures and mineral phases generated during both heating and cooling stages of sintering to be made. These results are then directly compared with the observation of the textures and phase assemblages present within an industrially-produced iron ore sinter. The comparative analysis between laboratory and industrial observations leads to a better understanding of how different operating conditions (e.g. atmosphere, temperature, cooling conditions) may impact on the final sinter mineralogy and microstructure.

2. Experimental Procedure

2.1. Sample Preparation

The starting materials for the iron ore sintering experiments were: a bulk iron ore blend, limestone, dolomite, silica sand, manganese ore, cold return fines (CRF) and New Zealand ironsand, supplied by BlueScope Ltd. The chemical compositions of the raw materials are reported in Ref. 14. Each raw material component, except the ironsand, was crushed and screened to less than 200 μm in size. These materials were then mixed in the proportion corresponding to that of BlueScope’s bulk sinter blend.

Five separate sinter blends were prepared with the CaO/SiO2 ratio varied from 1.5 to 4.0 so as to examine the effect of basicity on sinter phase formation. To these blends, 5 wt% of the ironsand was added and mixed to ensure homogeneity. The blend compositions are listed in Table 1. The final blends were pressed into cylindrical tablets of 5 mm diameter and ~5 mm height for sintering experiments, each weighing ~0.3 g.

2.2. Sintering

The laboratory sintering apparatus used in this study is described in detail elsewhere. The setup is based on a vertical tube furnace with a working diameter of 55 mm through which a gas mixture of controlled composition can be continuously passed. Experiments were conducted at a range of temperatures typical for iron ore sintering (1250, 1275, 1300 and 1325°C) and a range of gas compositions as shown in Table 2, for 4 minutes duration. A gas atmosphere of 1% CO-24% CO2-75% Ar mixture gives an equilibrium pO2 of 2.9×10^{-6} kPa (1250°C), 5.9×10^{-6} kPa (1275°C), 1.2×10^{-5} kPa (1300°C), and 2.3×10^{-5} kPa

<table>
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<tr>
<th>CaO/SiO2 ratio</th>
<th>Iron ore blend</th>
<th>Limestone</th>
<th>Dolomite</th>
<th>Silica sand</th>
<th>CRF</th>
<th>Ironsand</th>
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<td>6.5</td>
<td>1.9</td>
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<td>21.8</td>
<td>1.6</td>
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(1 325°C). pO₂ levels of 0.5 and 5 kPa were obtained by mixing Ar and air, and pO₂ of 21 kPa by using air. For each experiment the furnace was preheated to a designated temperature, and then purged with the relevant gas mixture for at least 20 min before a crucible with the specimen tablets was suspended in the hot zone of the furnace. After sintering for the desired time, the samples were then cooled following one of two procedures: (1) rapid cooling, where the crucible was directly lifted to the cold top end of the furnace tube while the gas mixture was kept unchanged; and (2) slow cooling, where the crucible was first lifted to a location in the furnace where the temperature was 1 160°C, and held there for 2.5 min before being lifted to the cold top end. The gas mixture was switched to purging air when the sample was lifted to the 1 160°C location.

2.3. Microstructure Analysis

The sintered tablets were mounted in epoxy resin, cut perpendicular to the top surface, and then polished for optical microscopic and SEM analysis. The optical microscope images were obtained in reflected light and analysed using Phase Expert software supplied by Leica. Different phases (hematite, magnetite and SFCA) as well as pores in the samples were identified by regions of homogeneous reflectivity. The various key phases were then differentiated by coloured overlays to show their distribution, and the volumetric fractions of the phases present in the sinter were determined using the software.

One point to note is that the software cannot distinguish between the silicate phase and sample pores due to similar reflectivities and therefore the presence of any silicate phase was not included in the determination of the mineral phases within the sintered samples. Another limitation of the software is that the image analysis results only report data for total SFCA (i.e. SFCA and SFCA-I) — the distinction between SFCA and SFCA-I can be made on a textural basis or by assessing powder X-ray diffraction data (i.e. SFCA and SFCA-I have distinct powder diffraction patterns), but automated identification is difficult using optical microscopy due to similarity in their compositions resulting in similar reflectivities. Hematite can be accurately identified by the software due to its sharp contrast with other phases. In comparison, there is not sharp contrast between SFCA and magnetite phases. Taking the image shown in Fig. 1(a) for instance, the uncertainty of the determined SFCA and magnetite phases is illustrated below.

Figures 1(b) and 1(c) present the same image processed using the software for determination of the volumetric fractions of SFCA and magnetite phases. Figure 1(b) was adjusted to minimise the apparent magnetite content and maximise the SFCA content, while Fig. 1(c) was adjusted oppositely. From Fig. 1(b), 29.3% of SFCA and 27.6% of magnetite were determined, while 26.4% of SFCA and 30.5% of magnetite were obtained in Fig. 1(c). Above data represents two extremes of the image analysis in the determination of phase compositions. The uncertainties of the volume fractions of SFCA and magnetite phases were ±5.2% and ±5.0%, respectively, relative to their volume fractions. The fraction of each phase was obtained by taking the average of 20 images with 200x magnification from each sintered sample. In general, the relative uncertainties of the volume fractions of SFCA and magnetite phases were in the range of ±5% of the corresponding values.
3. Experimental Results

3.1. Effects of Sintering Temperature and CaO/SiO$_2$ Ratio

To examine the effects of temperature and CaO/SiO$_2$ ratio (B) on sinter phase formation during heating, the ironsand-doped samples with different basicities (B = 1.5, 2.0, 2.5, 3.0 and 4.0) were heated at different temperatures (1250, 1275, 1300 and 1325°C) for 4 min in various gas mixtures (Table 2) followed by rapid cooling.

Figure 2 shows the optical images of samples with B = 2.0 sintered at different temperatures in a gas mixture containing 1% CO, 24% CO$_2$ and 75% Ar. As shown in Fig. 2(a), in the sample sintered at 1250°C, a significant amount (25.0%) of SFCA was formed. Under these conditions, most of the hematite was converted to magnetite (67.3%), although a small amount (7.7%) of unreacted hematite still remained. There was distinct aggregation and reaction of the finer ore grains resulting in the generation of sinuous pores, however at this temperature the assimilation of oxide materials was incomplete, leaving a large proportion of partially reacted iron ore and flux particles. There was little interaction of the ironsand particles with the other components with individual ironsand particles remaining largely unreacted.

When the sintering temperature was increased to 1275°C (Fig. 2(b)), the fine iron ore particles began to be assimilated through reaction with the flux components resulting in almost no discrete iron ore particles remaining. Magnetite (59.5%) was the dominant phase and the amount of SFCA formed reached a maximum (38.2%). Although the sample showed evidence of considerable reaction between components, the notable exception was the ironsand particles. While showing some evidence of reactive rims and partial assimilation, the bulk of the ironsand particles appeared to remain relatively inert during sintering.

The major phase (93.6%) present in the sample sintered at 1300°C (Fig. 2(c)) was magnetite, with textural evidence of secondary crystallised magnetite. Minor (6.4%) associated hematite was also present, however these were primarily relict hematite particles encapsulated inside magnetite par-

Fig. 2. Annotated optical reflected light images of specimens with CaO/SiO$_2$ ratio = 2.0 sintered at different temperatures for 4 min in a gas mixture containing 1% CO, 24% CO$_2$ and 75% argon followed by rapid cooling. H: Hematite; M: Magnetite; SF: SFCA; S: Silicates; I: Ironsand; F: Relict Flux. (a) 1250°C; (b) 1275°C; (c) 1300°C; (d) 1325°C. (Online version in color.)
articles. SFCA was less common and an interstitial silica-rich phase was also present. The ironsand still remained as large, mostly unassimilated particles.

Further increasing the sintering temperature to 1325°C (Fig. 2(d)) resulted in the disappearance of hematite and SFCA, accompanied by concomitant increases in the amounts of magnetite and silicate phases. Relict ironsand particles were still discernible as characterised by the presence of hematite exsolution lamellae in the cores. Even at this high temperature the original contours/shape of the ironsand particles remained clearly visible, although individual grains were intimately bound with other sinter components.

Figure 3 shows the volumetric percentage of SFCA (total) in specimens with B = 2.0 sintered at different temperatures and under different gas atmospheres, followed by rapid cooling. In general, at the same sintering temperature, more SFCA was formed in specimens sintered in gases with a higher pO2. In experiments at higher pO2 (21% and 5% O2) atmospheres, the amount of SFCA increased with increasing sintering temperature from 1250°C to 1300°C. Beyond 1300°C the amount of SFCA formed was significantly reduced. In comparison, in less oxidising or reducing conditions (0.5% O2 or 1% CO), the total SFCA content reached a maxima at 1275°C before becoming much less at higher temperatures.

Figure 4 presents the proportion of the three major phases, hematite, magnetite and total SFCA within specimens of varying basicity sintered at 1275°C and 1300°C and under two different gas atmospheres (0.5% and 5% O2, respectively), followed by rapid cooling. Overall, even though the temperature and pO2 were different, the proportion of all three phases followed similar trends with changing basicity. As the CaO/SiO2 ratio increased from 1.5 to 4.0, the content of SFCA increased, and there was a concomitant decrease in the amounts of both hematite and magnetite.

3.2. Effect of Sintering Gas Atmosphere

The previous results illustrating the effects of heating and CaO/SiO2 ratio on phase formation also indicated a pronounced effect of the gas atmosphere. To examine this further, Fig. 5 shows the measured phase proportions in

![Fig. 5. The phase composition of specimens sintered in different gas atmospheres for 4 min followed by rapid cooling.](image-url)
samples that were sintered in each of the four gas atmospheres (Table 2), followed by rapid cooling. Data are shown for three conditions: $T = 1275^\circ C$, $B = 2.0$; $T = 1300^\circ C$, $B = 2.0$; and $T = 1300^\circ C$, $B = 1.5$. The results indicate that the SFCA (total) and hematite contents both increased with increasing oxygen potential in the system, while the magnetite content decreased sharply. For example, SFCA was rarely detected in the sample with $B = 1.5$ sintered in a gas mixture containing 1 vol% CO-24 vol% CO$_2$ at 1300$^\circ$C, while the content of SFCA increased to >50% when the equivalent mixture was sintered in air. The specimen with $B = 2.0$ sintered at 1275$^\circ$C also increased in total SFCA content by nearly 30% as the gas atmosphere became progressively more oxidising. It should be noted, however, that the sample already contained a high amount of SFCA when sintered in a gas mixture containing 1 vol% CO-24 vol% CO$_2$.

Figure 6 presents the optical microscopic images of the specimens with a CaO/SiO$_2$ ratio of 2.0 subjected to sintering at 1300$^\circ$C for 4 min followed by rapid cooling. In a gas with 0.5% O$_2$, the sinter consisted of mainly primary and secondary magnetite; SFCA content was low and hematite was rarely found. Increasing O$_2$ to 5% resulted in more SFCA being formed, and some secondary hematite (which was formed by crystallisation of silicate melt during cooling) was identified together with primary hematite and magnetite. In the sample sintered in air, SFCA was the dominant phase with significant content of hematite; magnetite was rarely observed.

### 3.3 Effect of Oxidation during Cooling

The effect of oxidation on the sinter phase proportions was examined by comparing samples that were rapidly quenched, with those that were subject to a slower cooling profile. Figure 7 compares the phase proportions of the sinter specimens with $B = 2.0$ and sintered under four different gas atmospheres at 1300$^\circ$C, followed by either rapid cooling or slow cooling procedures. The results indicated that there was a negligible difference between the specimens sintered in air by rapid and slow cooling, with phase assemblages remaining approximately constant. In comparison, under more reducing gas atmospheres, there was a large difference between samples cooled by the two procedures. For rapidly cooled samples, the content of magnetite increased significantly with decreasing oxygen potential in the sintering gas mixture. However, this magnetite was almost totally eliminated during slow cooling for the sintered samples with 0.5% and 5% O$_2$. Correspondingly, the contents of SFCA and hematite both increased during slow cooling, and reached levels similar to those observed when the sample was sintered in air. For example, in the sample sintered in the gas mixture containing 0.5% O$_2$, up to 61.3% of magnetite was obtained by rapid cooling, whereas the amount decreased to only 2.9% following the slow cooling procedure. At the same time, the content of SFCA increased from 31.8 to 64.0%, and hematite from 6.9 to 33.0%.

Figure 8 compares the microstructure of two specimens with CaO/SiO$_2 = 2.0$ sintered in a gas with 0.5% O$_2$ at 1275$^\circ$C for 4 min followed by rapid cooling and slow cooling. It can be seen that the coalescence extent of the sample after slow cooling in air (Fig. 8(b)) increased significantly compared to the sample that experienced rapid cooling (Fig. 8(a)). Also, the sample after slow cooling was dominated by hematite and SFCA and contained almost no magnetite phase (main phase in the sample followed by rapid cooling).

### 4. Discussion

SFCA (including SFCA-I) is a calcium ferrite based mineral phase with aluminium and silicon. Considering the heating and cooling cycle of sintering, its formation starts with either CaFe$_2$O$_4$ (CF) or Ca$_2$Fe$_2$O$_5$ (C$_2$F) and recent work by Webster et al. indicates that in synthetic sinter mixtures, C$_2$F forms before CF. The pure CaFe$_2$O$_4$ phase has a melting point of 1216$^\circ$C while Ca$_2$Fe$_2$O$_5$ melts at 1449$^\circ$C. Due to the relative difficulty of solid state diffusion, formation of a localised melt enhances mass transfer and further reaction remarkably. Impurities such as silica...
and alumina within the sinter blend participate in additional reactions with the early formed ferrites resulting in the formation of SFCA phases.

In a relatively reducing gas atmosphere, decomposition of hematite to magnetite may take place:

\[ 2\text{Fe}_2\text{O}_3 = 4\text{Fe}_3\text{O}_4 + \text{O}_2 \]  

\[ 6\text{Fe}_2\text{O}_3 = 4\text{Fe}_3\text{O}_4 + \text{O}_2 \]  

Ignoring any kinetic impediment, whether Reaction (1) takes place is determined by temperature and the prevailing pO\textsubscript{2} for the reaction. In a CO and CO\textsubscript{2} containing gas, the equilibrium pO\textsubscript{2} may be determined by the thermodynamics of Reaction (2):

\[ 2\text{CO}_2 = 2\text{CO} + \text{O}_2 \]  

Figure 9 presents the equilibrium values of pO\textsubscript{2} for Reactions (1) and (2) in the 1% CO-24% CO\textsubscript{2}-75% Ar gas atmosphere calculated using the thermodynamic data from Ref. 17. It can be seen that the equilibrium pO\textsubscript{2} of the gas is six orders of magnitude lower than that of Reaction (1), which makes decomposition of hematite a highly favoured reaction throughout the temperature range examined in the investigation. The extent of this reaction is determined by kinetics. A pO\textsubscript{2} of 0.5 kPa (0.5% O\textsubscript{2} in gas) is insufficient to
supress the decomposition of hematite in the temperature range investigated. Below 1 230 and 1 290°C, Reaction (1) is suppressed by applying a pO2 of 5 kPa (5% O2 in gas) and 21 kPa (air), respectively.

Dissolution of limited amounts of silica and alumina in the CF and C2F phases (as in the case of the formation of SFCA phases) decreases their melting temperatures. The formation of a melt from SFCA could then occur for two different reasons: (1) a physical melting process without a chemical reaction involved, or (2) reduction of Fe3+ to Fe2+ in SFCA which affects its stability. A single-phase SFCA was prepared containing 77.4 wt% Fe2O3, 14.1 wt% CaO, 3.6 wt% SiO2 and 5.0 wt% Al2O3. The starting mixture of the single-phase SFCA sample was sintered at 1 100°C for 48 hours in a muffle furnace and XRD analysis confirmed the sample contained only SFCA phase. The SFCA and a chemically pure hematite sample were tested by TG-DSC analysis at a ramping rate of 10°C/min in argon and in air using high-purity alumina crucibles with an internal diameter of 5 mm. Figure 10 shows the TG-DSC patterns of hematite and the single-phase SFCA heated at 800–1 450°C in air. It is noted that the SFCA sample started to lose weight at 1 220°C in air, which was significantly lower than the temperature the hematite started to lose weight, which was measured to be at 1 335°C. The total weight loss of the hematite sample was about 3.0 wt% which is close to the theoretical value of 3.3 wt% if the hematite was completely decomposed in the SFCA crystal structure to Fe2O3.

The synthetic SFCA was also heated at a rate of 10°C/min, under a flow of air. The content of SFCA was decomposed in the SFCA sample in comparison with that in the hematite sample. During this heating process, the hematite sample did not melt because the maximum temperature (1 450°C) of the test is much lower than the melting points of pure hematite and magnetite. For the SFCA sample, however, besides decomposition of Fe2O3 in SFCA phase, a melt is believed to have been generated due to the larger heat flow in the DSC pattern accompanying the weight loss. The total heat flow calculated from the SFCA curve was 0.365 J/mg-Fe2O3, while the total heat flow calculated from the hematite curve was only 0.240 J/mg-Fe2O3.

The synthetic SFCA was also heated at a rate of 10°C/min, under a flow of air. The content of SFCA was examined by in situ XRD, and the XRD data were collected over the range 10° ≤ 2θ ≤ 120° continuously throughout heating, with individual datasets collected for 0.5 min. The use of the diffractometer and high-temperature chamber in an iron ore sinter phase context has been described previously.11,12) In this case, however, the concentration of the gas exiting the high-temperature stage was measured using a Thermo Scientific VG PROLAB Benchtop QMS, and Fig. 11 shows the variation in the SFCA scale factor, and the O2 concentration in the exit gas, as a function of temperature. The spike in the O2 concentration occurred corresponding with a decrease in the SFCA scale factor (i.e. the decomposition of SFCA), which is interpreted as being indicative of the reduction of Fe3+ in the SFCA crystal structure to Fe2+.

In the sintering process, if a specimen is heated to a temperature sufficient to form a liquid phase, on subsequent cooling, the melt will convert to a glassy phase and secondary magnetite in a reducing atmosphere, or form SFCA phase and secondary hematite if enough cooling time is provided in an oxidising atmosphere.

The nominally isothermal sintering process was practically a rapid heating process, with a heating rate significantly faster than that used by Webster et al.11) As shown in Fig. 2(a), SFCA was present in the bonding matrix of the specimen sintered at 1 250°C in an atmosphere of 1% CO-24% CO2 followed by rapid cooling. The contours of the original particles remained, indicating a lack of assimilation, although a small portion of magnetite was identified as having been crystallised from a melt (secondary magnetite) which means that local melting took place during sintering (e.g. in areas close to a flux particle where the local CaO/SiO2 ratio was very high). At this relatively low temperature, SFCA was formed via solid state reactions among iron ore, flux, and alumina and silica impurities.11,15–17) It can be expected that the magnetite phase in this sintered sample was from the decomposition and melting of SFCA and, mostly, from decomposition of hematite. The presence of hematite phase encapsulated in the magnetite particles suggests that its decomposition was still incomplete. A lack of glassy phase is an indication of insignificant melting of SFCA.

An increase in temperature from 1 250 to 1 275°C in a reducing atmosphere resulted in the formation of more
SFCA phase (Fig. 2(b)). Secondary magnetite particles were also observed in this sample, meaning that a significant amount of melt phase was formed during heating.

A further increase in temperature to 1300 and 1325°C almost completely eliminated SFCA whereas there was a significant increase in the amount of magnetite and glassy silicate phases. At these temperatures, SFCA phases are unstable, and incongruently melt to form the assemblage of magnetite and a melt.11) As shown in Figs. 2(c) and 2(d), the amount of secondary magnetite also increased along with increasing temperature, indicating more severe melting of SFCA at these temperatures. Rare hematite was found located inside the iron ore matrix surrounded by magnetite. This hematite residue was not reduced to magnetite due to lack of exposure to the gas atmosphere.

As shown in Figs. 3, 5 and 6, increasing the partial pressure of O₂ in the sintering gas atmosphere significantly increased the content of SFCA in a sinter specimen because it increased the stability of SFCA at higher temperatures, which is consistent with the observation by Webster et al.12) When the temperature went beyond 1300°C, the pO₂ was not high enough to fully suppress the decomposition of SFCA, resulting in decreased SFCA content in the sinter samples. This brought about a maximum SFCA content at a temperature which increased with increasing pO₂. As shown in Fig. 6(c), in the sample sintered in air at 1300°C, the sinter consisted of mainly SFCA and hematite; magnetite was rarely observed. Because the melting of SFCA was accompanied by reduction of Fe₂O₃ in this phase to magnetite, reoxidation of the latter must have taken place in order to form secondary hematite and SFCA phases during cooling in air.

It is also noted that, although a higher pO₂ favoured SFCA formation by solid-state reaction at lower temperatures e.g. 1250°C, the assimilation of original blend particles was more complete with a more reducing gas atmosphere. It is mainly because FeO fluxes calcium ferrite phases to form melt at lower temperatures, which promotes mass transfer and assimilation reactions between solid particles via the melt. This is illustrated in Fig. 12 where the CaO–Fe₂O₃–FeO phase diagram18) indicates that the liquidus temperature decreases gradually with the introduction of FeO into CF or CF₂.

High basicity favours formation of SFCA, as demonstrated by Fig. 4. As shown in Reaction (1), increasing the content of CaO (as formed by decomposition of limestone) enhances the formation kinetics of calcium ferrite by solid state reaction at low temperatures; at high temperatures when SFCA is crystallised from a melt phase, a high concentration of CaO also favours formation of SFCA via thermodynamics and kinetics. As a result, the content of SFCA increased consistently with increasing the CaO/SiO₂ ratio of the sinter blend at different sintering conditions.

The morphology of a commercial sinter supplied by BlueScope was also examined in this study. This sinter contained approximately 23% SFCA (total), 6% primary hematite, 31% secondary hematite, 25% magnetite and 15% silicates, as analysed by traditional point counting method. Figures 13(a) and 13(b) show typical microstructures from the exterior and interior of lumps of this commercial sinter, respectively. The exterior of the sinter has similar morphology to that of laboratory sinter following the slow cooling procedure presented in Fig. 8(b). In comparison, a large amount of magnetite and interstitial silicates were observed in the interior of this commercial sinter, which is similar to the laboratory sinter sintered in a reducing atmosphere as shown in Figs. 2(c) and 2(d). It is known that the reaction conditions in an industrial iron ore sintering process are heterogeneous. Generally, in the heating stage the iron ore...
particles are in a more reducing atmosphere, while in the cooling stage, the particles adjacent to the gas flow channels are subject to a highly oxidising atmosphere. From the above similarity in the microstructure of commercial sinter shown in Fig. 13 with that obtained in the laboratory presented in Fig. 8(b), as well as the similarity in the changing patterns of the sintering conditions, it can be recognised that the SFCA phase in commercial sinter is most likely formed by heating the sinter blend in a relatively reducing atmosphere followed by cooling in an oxidising atmosphere.

In this investigation, the smaller size of raw material particles and continuous void generated during heating in addition to the relatively small tablets used benefit the diffusion of gas mixture inside a specimen. Therefore the reactions in laboratory sinter were more homogeneous and susceptible to a greater influence of the prevailing gas atmosphere. Accurately controlled experimental conditions and uniform reactions during sintering however are helpful to reduce the uncertainty and better investigate the effects of sintering conditions on the final mineralogy of sinter.

5. Conclusions

The effects of sintering temperature, CaO/SiO₂ ratio, sintering gas atmosphere and cooling procedure on the formation of mineral phases during iron ore sintering were examined with focus on the formation of SFCA phases to gain a better understanding of the sintering mechanism of iron ores, which is helpful for controlling the quality of final sinter. The main results obtained are summarised as follows.

1. The content of SFCA phase was significantly affected by temperature. In the temperature range of 1250–1300°C, SFCA formation was enhanced by increasing temperature. Further increasing sintering temperature promoted the reduction of Fe³⁺ in the SFCA crystal structure to Fe²⁺ and consequent decomposition of SFCA.

2. Sintering at a low temperature generated SFCA by solid state reactions. At high temperatures, SFCA was produced during cooling via crystallisation from a silicate melt. Slow cooling in an oxidising gas atmosphere strongly promoted formation of SFCA.

3. Increasing CaO/SiO₂ ratio and oxygen partial pressure favour the formation of SFCA phase. A high oxygen partial pressure suppressed conversion of hematite into magnetite, and so promoted formation of SFCA.

4. A typical microstructure of SFCA bonding phase in the commercial sinter was formed by crystallisation from a silicate melt formed in the heating stage with relatively low oxygen partial pressure, during cooling in an oxidising gas atmosphere.

Acknowledgements

The project is financially supported by the BlueScope Steel Metallurgical Centre Projects Grant. The authors would like to acknowledge the Electron Microscopy Center (EMC) at University of Wollongong for SEM/EDS analysis.

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