PHASE RELATIONS IN THE MAGNETITE CORE OF IRON ORE PELLETS[1]

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Abstract

During the induration of pellets produced from magnetite concentrates, oxygen access to the core is restricted while slag formation is occurring. This situation is analogous to what happens in the core of pellets produced from hematite concentrates with added carbon, where significant amounts of secondary magnetite are formed from hematite being reduced. Individual green balls and compacts of ground magnetite ore, limestone flux, silica and carbon were fired at precisely controlled temperatures to determine what slag phases formed at that temperature, especially in the core. In some cases, more silica and lime was added than in real pellets to produce larger quantities of slag that were easier to characterise. Optical and scanning electron microscopy showed that the lack of oxygen in the core of the pellets results in the onset of calcium silicate slag formation at lower temperatures, around 1100 °C. The initial slag may not be fully molten, however, as the slag phase does not cover the particles until the temperature exceeds 1250 °C. The quicker onset of slag formation in the core often results in greater sintering than in the shell of the pellet, causing the core to pull away. As a result, low compressive strengths are obtained.

Key words: Iron ore pelletising; Pellet mineralogy; Thermodynamics.

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INTRODUCTION

Since the late 1970's(1) internal carbon sources such as coke breeze and anthracite have been added to pellets produced from hematite ores and concentrates. In Brazil, fine charcoal was also tested as a potential carbon addition.(1,2) The intention of adding carbon was to provide an internal heat source for the pellets, reducing the firing temperature necessary for sufficient strength. A way of thinking of added internal carbon is in terms of "magnetite equivalent" with 1.56%(3) carbon by mass being equivalent to 100% magnetite. Adding carbon beyond 100% equivalent magnetite results in low strength pellets with a high Fe^{2+} content due to remnant magnetite cores.

While adding internal carbon at quantities close to 100% magnetite equivalent does reduce the energy requirements for induration of hematite pellets, the energy is released in two stages over most of the pellet. In the core of the pellet, where the oxygen supply is limited, the carbon partially combusts to carbon monoxide. The carbon monoxide then reacts with the hematite, reducing the particles to "secondary" magnetite. This gives rise to a "duplex" structure in the pellet part way through firing that is very similar to that in partially oxidised magnetite pellets where a hematite shell surrounds a magnetite core.(4) Later in the firing process when all the carbon has reacted, the magnetite oxidises, releasing heat in the process.

For most pellets in a pelletising process, there is still a significant magnetite core when firing temperatures, above 1200 °C, are reached and liquid slag phases form. As the oxygen is consumed at the reaction front between hematite and magnetite, the gas in core of the pellet becomes deficient in oxygen compared to the outer hematite shell. This causes different microstructures to form in the core of the pellet compared to the outer regions.(5-8) In extreme cases, the core of pellet can become more sintered than the outer shell and pull away from it, leaving concentric and radial cracking. This causes the pellet compressive strength to drop rapidly and is generally interpreted by plant operators as over-firing, requiring correction by decreasing the temperature setpoint in the firing zone or reducing the internal carbon addition. It follows that much of the microstructure difference is due to the higher amount of slag formed in the core compared to the outer zone of pellets. More slag forms in the core of pellets as the lack of oxygen allows the liquid phase to form at lower temperatures.

The phase relationships of slag phases in pellets are not well understood outside of purely oxidising conditions(9) due to the transient nature of the oxygen potential and the inability to measure the oxygen potential within the pellet. The objective of this research is to categorise the phase relations in the magnetite core of iron ore pellets and to draw conclusions from observations from firing magnetite pellets. For further analysis on the mineralogy and properties of hematite pellets with added carbon fuel, the studies by Wilhelmy *et al*(8) and Audet *et al*(3) give a good background.

METHOD

For the initial single pellet tests, a 20 kg batch of green balls was prepared from an industrial magnetite concentrate, with added limestone and dolomite fluxes and 0.07% bentonite used as the binder. The magnetite concentrate and the fluxes were ground to 85-90% -38 µm and mixed together in a batch balling drum. The target chemical analysis of the fluxed pellets (calcined) was 65.3% total Fe, 2.4% SiO_2, 2.4% CaO, 1.4% MgO and 0.14% Al_2O_3.

After being dried in an oven at 105 °C for 16 hours, the individual green balls were heated using a QHC-E44 VHT infra-red image furnace produced by Ulvac-Riko Inc. The furnace uses gold-plated parabolic mirrors to focus infra-red radiation on the hot zone, allowing close control and rapid changes in temperature (Figure 1). The atmosphere of the furnace was controlled at an air composition (79% N_2 and 21% O_2), slightly higher than normal gas composition during firing but useful due to the large amount of thermodynamic data available at this oxygen concentration. Rapid quenching of the samples was performed using a high flowrate of nitrogen gas. The test method used here was originally developed by Firth(10) for the evaluation of firing profiles for pellets produced from Australian magnetite concentrates.

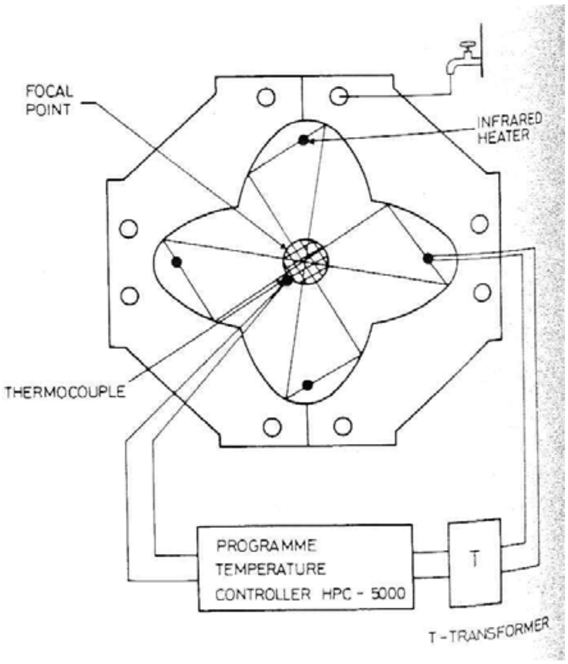

Figure 1. Schematic of an infra-red image furnace

Single green balls of a suitable size, about 12.5 mm in diameter, were placed in a nickel foil crucible before being place in the furnace with an R type thermocouple (platinum – platinum-10% rhodium) used to measure the surface temperature of the pellet. Once the pellet was in place, its surface temperature was increased to 240 °C in 4 minutes, then to the desired firing temperature (between 1000 and 1200 °C) in 3 minutes. This profile was used to approximately simulate the average temperature ramp experienced by pellets in the bed of the grate section of a grate-kiln induration furnace(9), although the ramp to the preheat temperature is also similar to that experienced by pellets on their way to firing temperatures in straight grate furnaces. While holding the individual pellet at a specific temperature does not correlate directly to the pellet induration process, this method allows local equilibrium of the pellet microstructure and phase transformations to be linked to a specific temperature range. After 3 minutes at the desired temperature (1000, 1050, 1100, 1150 and 1200 °C), the run was terminated and the pellet was quenched immediately in nitrogen.

Four pellets were fired at the same conditions, mounted in epoxy resin, sectioned at the approximate centre-line of the pellets, and then polished flat to a surface finish of 1 µm. These pellets were then analysed microscopically under reflected light at a variety of magnifications. Selected samples were also assessed by electron probe microanalysis (EPMA) with both point compositions and element maps being collected. Quantitative analysis of the composition of the slag generated during preheat was difficult as the pools of slag were very small and the composition given by EPMA was influenced by the nearby iron oxide phase.

To increase the size of the slag pools that formed, it was decided to produce cylindrical compacts of a similar size to pellets with higher limestone and silica contents than would normally be used (5 and 10% silica). Compacts were made rather than pellets to reduce the raw material requirements of the testwork as phase compositions were to be assessed rather than phase assemblage. The magnetite concentrate used for the compacts (before silica and limestone addition) was very high in grade (70.1% total Fe, 1.45% SiO_2, 0.11% CaO, 0.33% MgO and 0.03% Al_2O_3). Reagent grade silica and high purity limestone were the only additives used to simplify the reaction system, excluding aluminium and magnesium as much as possible. The basicity (CaO/SiO_2) level studied was 1.2, a typical basicity for fluxed blast furnace pellets.

As slag formation in the core of the pellet was the focus of our study, a bottled gas mixture of 0.5% oxygen in nitrogen was used ($p_{O2} = 5 \times 10^{-3}$ atm). This gas atmosphere has been used extensively by CSIRO Minerals for its work into melt formation at the flame front in iron ore sintering.(11) At this oxygen partial pressure, magnetite is the stable iron oxide phase between 1100 and 1225 °C. The compacts were heated following the same profile as the individual pellet tests in the infra-red image furnace. They were held at the maximum temperature for 20 minutes to ensure good local equilibrium between the materials and so as to ensure the formation of large areas of slag for EPMA point analysis. Qualitative equilibrium results in terms of phases present can be interpreted from these tests but experiments at a smaller scale with longer equilibration times would be required for proper quantitative phase diagram development. The reason for this methodology is to determine the trends in phase compositions that occur in the firing of real iron ore pellets.

RESULTS FOR FLUXED PELLETS

A series of single pellet firing experiments with normal blast furnace fluxed pellets ($CaO/SiO_2 = 1.2$) were conducted. While the pellets were made from magnetite concentrate, the microstructures observed would be valid for hematite pellets with high carbon addition typical of current Brazilian and Canadian(3) practice. The pellets were held at the preheat temperature for 3 minutes, a time that is insufficient to oxidise all the magnetite resulting in a remnant core.

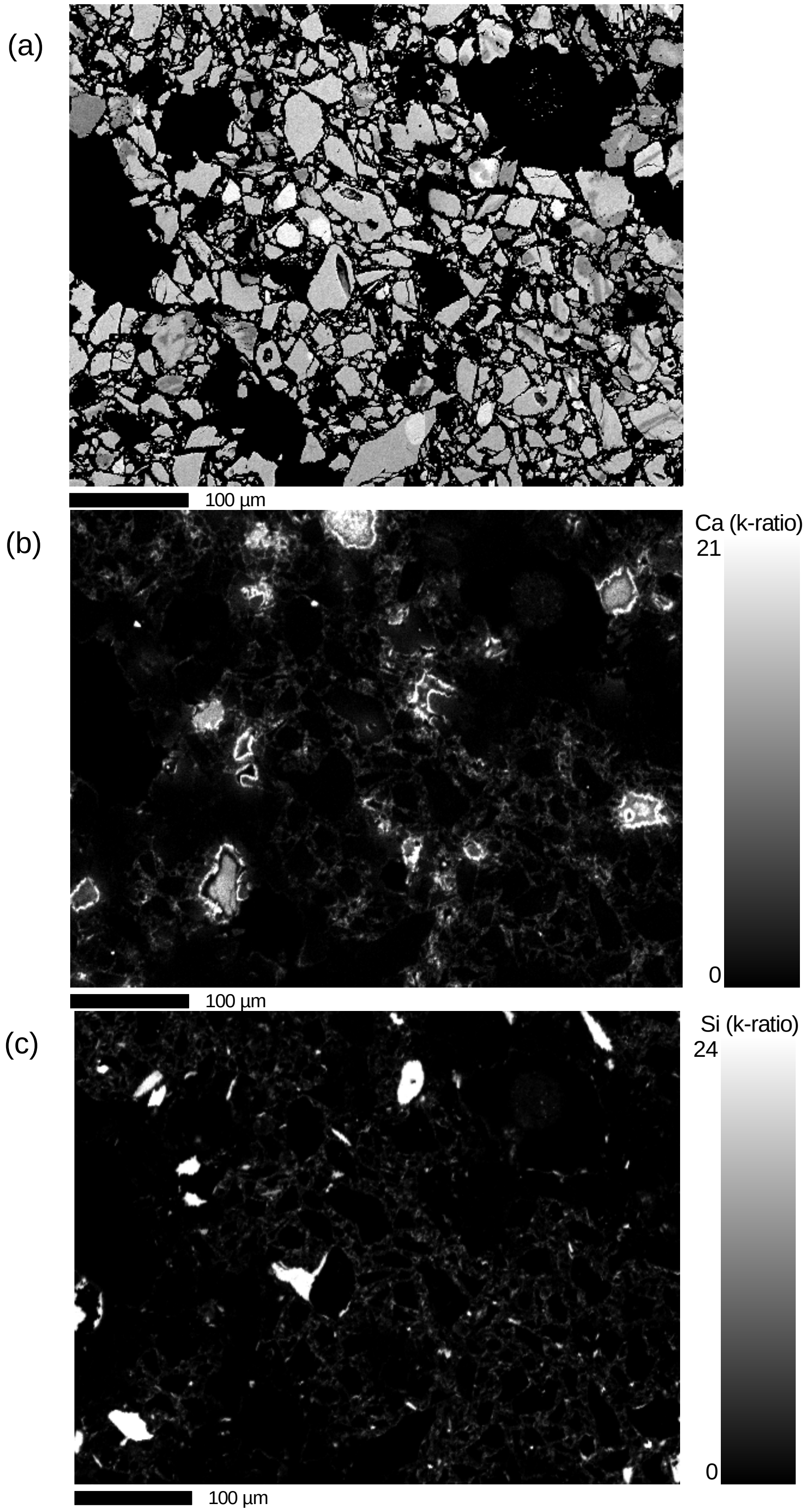

Figure 2. Maps generated by EPMA of a pellet heated at 1050 °C for 3 minutes in air. The maps were taken in the magnetite zone near the oxidation front in the pellet. (a) shows the electron backscatter map, with hematite grains darker than the magnetite, (b) shows the calcium distribution and (c) shows the silicon distribution. k-ratio give the mass percent of the element with the scale bars at right indicating their relative concentration for each.

At 1000 °C, it was observed that the silicon and calcium had only just started to react. A small amount of calcium had reacted with the iron oxides to form dicalcium ferrite ($Ca_2Fe_2O_5$), predominantly in the re-oxidised secondary hematite zone as calcium is partially soluble in the magnetite.

At 1050 °C, the observations are similar to 1050 °C except that the dicalcium ferrite is now more widespread and calcium has dissolved in the magnetite up to a concentration of 2%, mainly in the regions around ex-flux particles. Silica particles do not appear to have reacted with the calcium as yet, except directly next to flux particles. The distributions of key elements such as Ca and Si are provided in Figure 2.

At 1100 °C, especially in the reduced core of the pellet, there is evidence of significant reaction between calcium and silica, and most likely with the iron oxides as well. This is most abundant in the magnetite core of the pellet. In particular, there is evidence of dissolution of parts of the large silica grains into a calcium- and silicon-rich phase.

At 1150 °C, (Figure 3), the areas containing both silica and lime have become more numerous compared to 1100 °C, although they are still quite small. Some small areas of slag also appear to have been trapped within hematite grains as the oxidation front has passed through. These trapped slag regions often appear to have a lower calcium to silicon ratio compared to slag in other areas. Due to the small size of the slag grains however, it is difficult to measure the compositions of the various slag morphologies. These trapped slag regions are common in pellets produced industrially from both hematite(8) and magnetite(6) concentrates.

At 1200 °C, an iron calcium silicate melt has formed in both the oxidised hematite shell and reduced magnetite core of the pellet. While it was has previously been suggested that the composition of the melt might vary between oxidising and reducing atmospheres,(12) this was difficult to determine in practice. The fields of slag are typically very small and quantitative point analysis by EPMA invariably has some interference by the nearby iron oxide, increasing the apparent iron content.

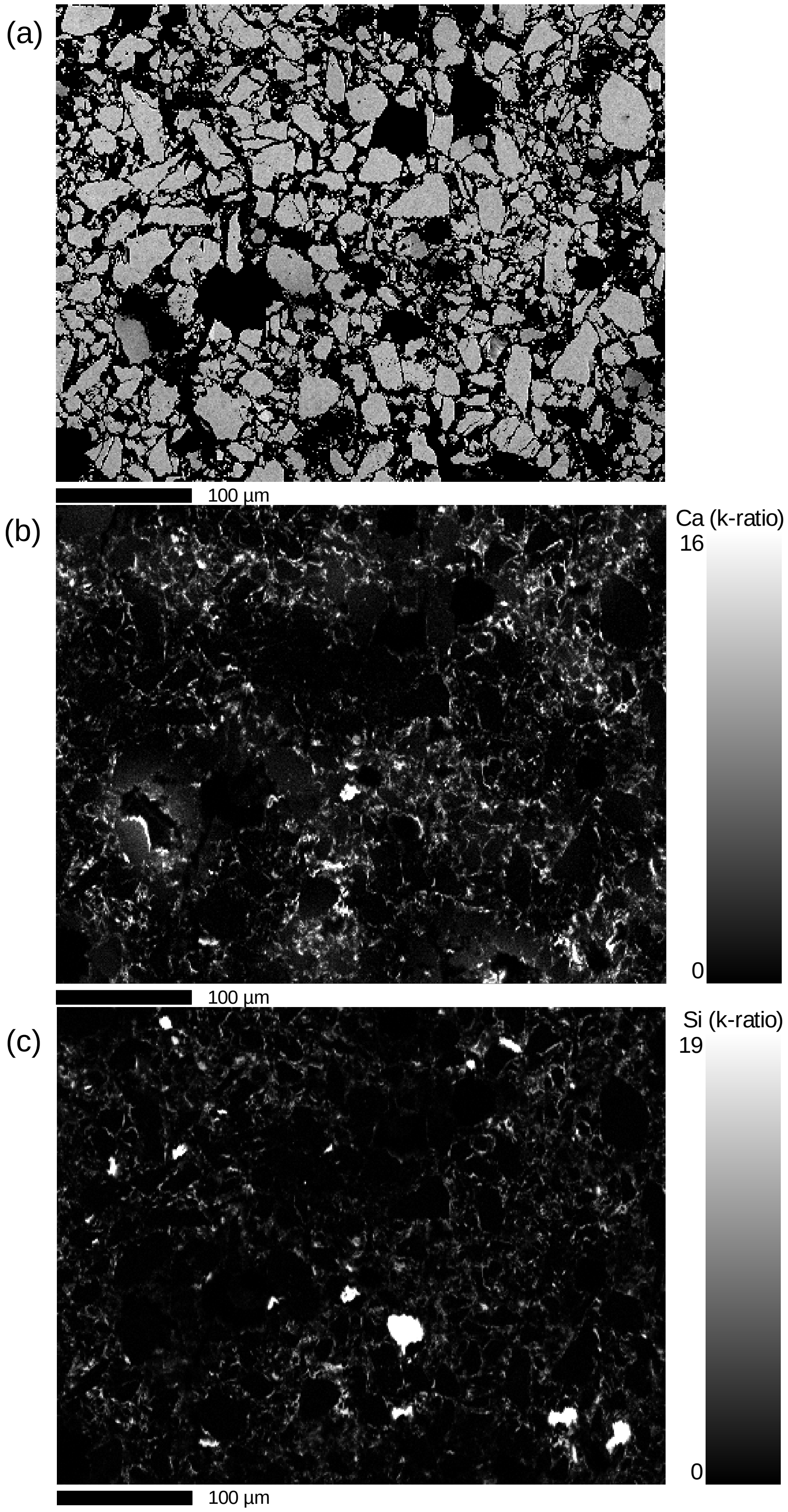

Figure 3. Maps generated by EPMA of a pellet heated at 1150 °C for 3 minutes in air. The maps were taken in the magnetite zone near the oxidation front in the pellet. (a) shows the electron backscatter map, with hematite grains darker than the magnetite, (b) shows the calcium distribution and (c) shows the silicon distribution. k-ratio give the mass percent of the element with the scale bars at right indicating their relative concentration for each.

RESULTS FOR COMPACTS WITH REDUCED OXYGEN

Motivated by the inability to determine accurate quantitative flux compositions, subsequent experiments using cylindrical compacts to save on material preparation were performed where the samples were held at temperature for 20 minutes in an atmosphere with an oxygen partial pressure of 0.005 atm. At this oxygen partial pressure, magnetite is the stable iron oxide, similar to the situation in the core of iron ore pellets. We also used cylindrical compacts, formed under pressure for the experiments, rather than pellets as we wished to use compositions higher in lime and silica than typical pellets in order to generate larger slag pools for probing.

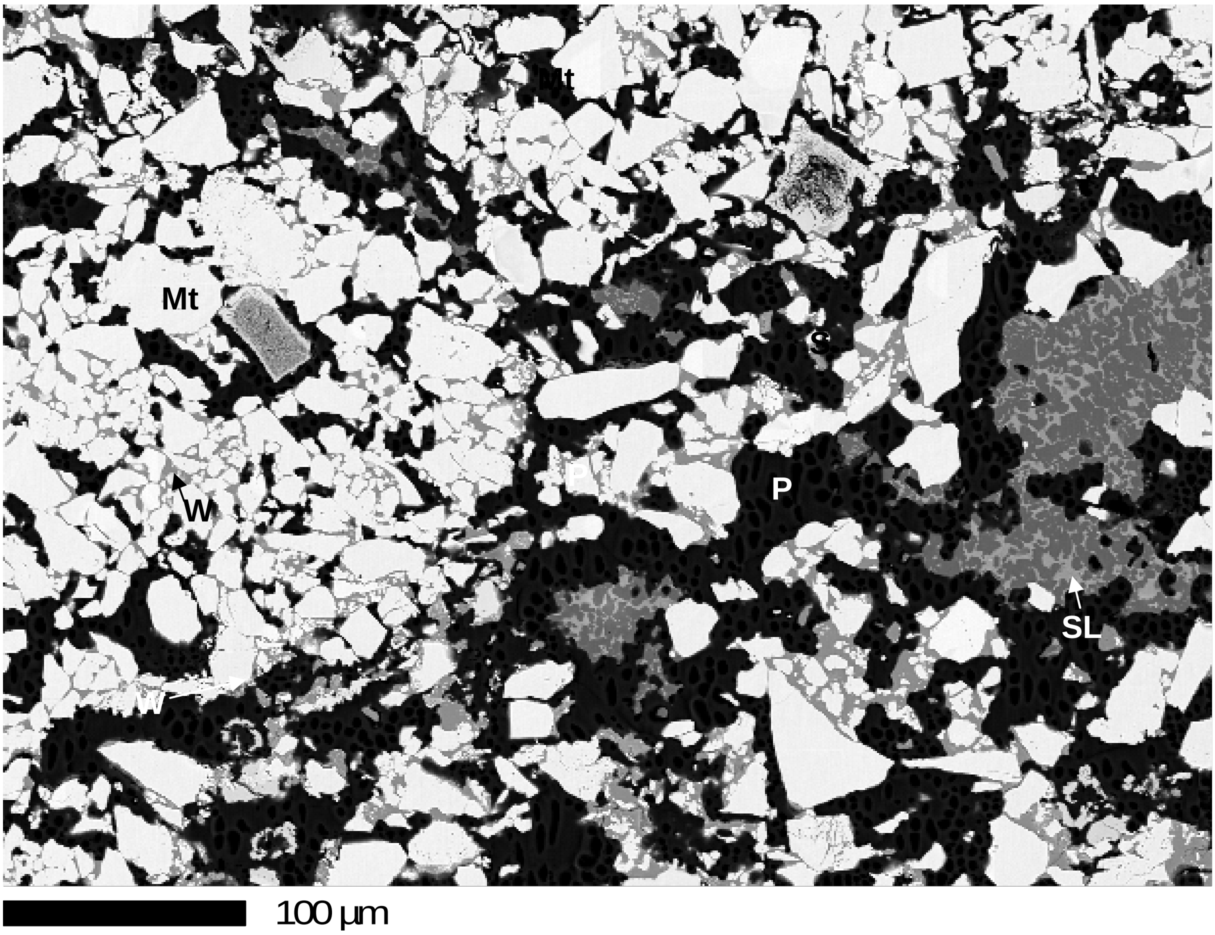

Figure 4. Electron backscatter image of a magnetite compact with 10% SiO_2 and 12% CaO fired at 1100 °C for 20 minutes. Mt denotes magnetite, SL denotes eutectic slag dissolving a silica particle (S), W indicates the wollastonite remnant of the slag from cooling, P denotes a pore.

Element maps and individual point probing by EPMA revealed that a small amount of liquid slag can form in the absence of oxygen at temperatures as low as 1000 °C. This slag was only found to be present within silica grains at that temperature. A typical composition of the slag was 24% Si, 16% Ca, 17% Fe and 43% O which is close to the quaternary eutectic in the CaO-FeO-Fe_2O_3-SiO_2 slag system(13). Note that there may have been some alteration away from the eutectic composition on cooling. The melting point of this eutectic is 1093 °C(13). There was some wollastonite ($CaSiO_3$) appearing interstitially between the magnetite grains as a molten slag would (Figure 4). It was assumed that this wollastonite phase was richer in iron while at 1100 °C, similar in composition to the eutectic melt, and during the quenching process the dissolved iron oxide was absorbed by the surrounding magnetite. The closeness of the eutectic melt composition to the wollastonite solid solution line backs up this possibility. Close to remnant particles of lime with dicalcium ferrite ($Ca_2Fe_2O_5$) and larnite (Ca_2SiO_4) also appear in the quenched pellets. Dicalcium ferrite is the stable calcium ferrite at this oxygen potential and temperature while the larnite probably precipitated from a melt during the quenching process.

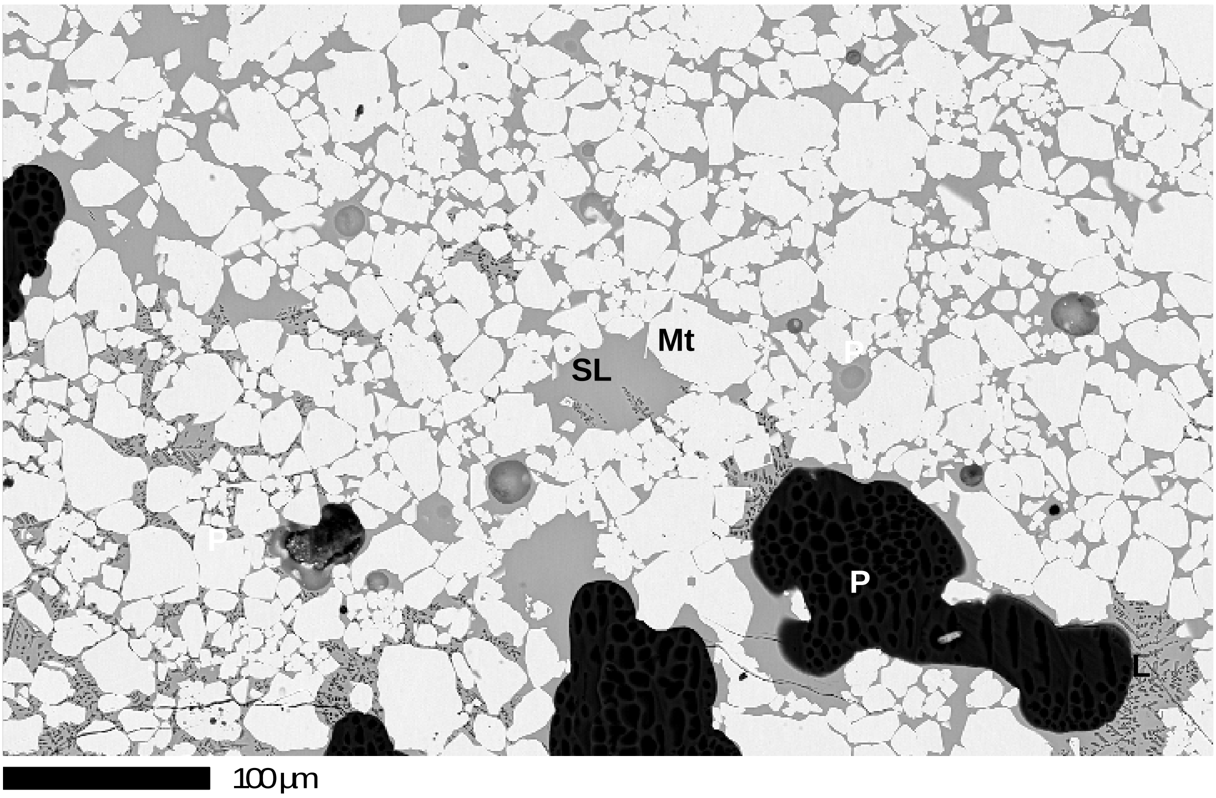

Figure 5. Electron backscatter image of a magnetite compact with 10% SiO_2 and 12% CaO fired at 1175 °C for 20 minutes. Mt denotes magnetite, SL denotes eutectic slag, L indicates larnite precipitating from the slag on cooling, P denotes a pore.

At temperatures above 1150 °C, the eutectic slag becomes widespread between the magnetite grains, allowing significant sintering to occur (Figure 5). This is different to the outer hematite zone of the pellet where significant molten slag formation does not occur until around 1200 °C$^{(10)}$. Note that Figure 5 exaggerates the amount of slag formed due to the longer time at temperature and higher gangue composition compared to real iron ore pellets. Figure 5 does, however, indicate the chemical equilibrium between the magnetite core and the slag that would develop given enough time at 1175 °C. The typical slag composition recorded from EPMA point analysis was 1% Mg, 21% Si, 25% Ca, 14% Fe and 39% O. Compared to the slag obtained at 1100 °C, it had now fully dissolved the calcium and silicon oxides and was sitting at a higher liquidus temperature, again near the wollastonite solid solution line. It is thought that some of the iron oxide precipitated from the slag and grew onto the magnetite particles during cooling, reducing the apparent iron content of the slag. In some slag pools, particularly at temperatures over 1175 °C, magnetite precipitated directly out of the slag in the form of fine dendrites. This was often accompanied by coarser dendrites of larnite (Ca_2SiO_4) precipitating, which can be seen in parts of Figure 5. The precipitation of magnetite and larnite from the slag during quenching suggests that the composition determined from point probing of the slag pool might be slightly different to that at temperature. The elimination of small pores from Figure 4 to 5 is also of note, showing the extent of sintering behaviour and the influence of the level of slag formation in pellets on reducibility.

CONCLUSIONS

In the reduced cores of iron ore pellets, either produced from magnetite concentrates or hematite ores with internal carbon addition, the formation of iron-calcium silicate slag occurs at significantly lower temperatures compared to the oxidised shell of the pellet. There is evidence for the early stages of slag formation around 1100 °C, with full slag forming around 1150 °C. By contrast, full slag does not appear in the oxidised hematite shell of the pellets until around 1200 °C and some slag originally formed near magnetite tends to become trapped within the hematite grains after the oxidation front moves through. This reflects the difference in melting point in the lime-silica-iron oxide system for different oxygen potentials.

The importance of understanding the different slag forming behaviours between the core and shell of pellets is due to the influence of slag formation on the sintering process between the iron oxide grains. The sintering process generates the required strength in the fired pellets. When a large magnetite core exists at firing temperatures, more slag is formed in the core compared to the shell of the pellet due to the absence of oxygen. This helps the core become more sintered than the shell and leads to the core pulling away, resulting in internal concentric and radial cracks appearing in the pellet. Such cracks significantly reduce the compressive strength of the pellet and the appearance of these cracks is generally considered a sign of “over-firing” by pellet furnace operators. Better understanding of slag formation and its influence on pellet strength will allow better optimisation of pellet induration.

Acknowledgements

The assistance of staff at the CSIRO Minerals electron microscopy facility, specifically Nick Wilson, Colin MacRae and Cameron Davidson during this investigation was greatly appreciated. Abebe Haileslassie is thanked for his assistance with the preparation of the polished blocks. Ross Price is thanked for his assistance in preparing the green balls.

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