CHARACTERISATION AND REDUCTION OF HIGH-SILICON IRONSTONE ORE BY CO GAS

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ABSTRACT

Ironstone ore can be a valuable source of iron and silicon in production of silicomanganese and other alloys. This paper provides analyses of the chemical and phase composition of ironstone and information on the reduction of ironstone by carbon monoxide at temperatures in the range 800 to 1150°C. Ironstone was provided as a crushed ore and a lumpy ore. Crushed ironstone ore contained higher Fe_2O_3 concentration (40.6 wt %) and lower SiO_2 content (44.3 wt%) compared to the lumpy one (21.2 wt % Fe_2O_3, 68.9 wt % SiO_2).

Phases in the ore detected by XRD and SEM/EDS analyses were hematite and quartz. Two major reactions were observed upon heating ironstone in CO atmosphere, namely; partial reduction of iron oxides and formation of fayalite. The rate of fayalite formation increased with increasing temperature. Ore porosity significantly decreased upon heating. Ore softening and partial melting started at 1100ºC-1150ºC with a significant negative effect on iron oxide reduction. The weight loss of the crushed ore increased with increasing temperature to 1000°C and decreased when temperature increased further to 1150ºC. The weight loss of the lumpy ore decreased with increasing temperature from 1100ºC to 1150ºC. Based on LECO analysis, the degree of iron oxide reduction in the crushed ore was estimated 82.4% at 1000ºC, 68.8% at 1100ºC and 33.1% at 1150ºC. The degree of iron oxide reduction in the lumpy ore was 79.5% at 1000ºC, 82.7% at 1100ºC and 47.2% at 1150ºC. No metallic iron was detected by XRD in samples heated in CO atmosphere at 1150ºC, although a small amount of metallic iron was observed in SEM/EDS analysis.

KEYWORDS: *Ironstone, phase composition, reduction, carbon monoxide.*

1. INTRODUCTION

World iron ore production in 2011 reached 2,800 Mt (U.S. Geological Survey, Mineral Commodity Summaries, January 2012), 98% of which was used to produce 1,490 Mt of steel (World Steel Association – Steel production 2011, www.worldsteel.org). Iron in the iron ore is usually found in the form of magnetite (Fe_3O_4), hematite (Fe_2O_3), goethite (FeO(OH)), limonite ($FeO(OH).n(H_2O)$) or siderite ($FeCO_3$). High quality ore with more than 60 wt% iron oxide is directly used in ironmaking; while majority of ores need beneficiation. Gangue materials of iron ores contain silica, alumina, calcia and other impurities.

Tasmanian (Australia) ironstone ore which is examined in this paper is rich in iron and silicon. It can be a valuable source of both iron and silicon in production of silicomanganese and other alloys. Reduction of iron oxides from hematite, goethite, limonite and magnetite ores was studied in numerous papers [1-9]. Reduction of iron and silicon oxides from ironstone ores has not been examined. The ore reduction behavior depends on the ore mineralogy and morphology and their

change in the process of heating and reduction. This was demonstrated by Turkdogan et al. [7] in their study of the effect of lime addition on the reduction of pellets of a high-grade iron ore in CO and H_2. They found that blockage of pores took place in the ore by molten calcium ferrite which was formed during pellets sintering. St John et al. [3] observed morphological changes upon ore heating from 600°C up to 1100°C.

Based on thermodynamic analysis, the reduction of pure iron oxide tends to go to formation of sub-oxides and eventually metallic iron at temperatures below the melting point of oxides and iron. However, upon heating ironstone ore, low-melting phases can be formed with a negative effect on the ore reduction behavior.

The aim of this paper has been to study the chemical and phase composition of Tasmanian ironstone ore and their change upon heating in different gas atmospheres in the temperature range 800 -1150°C.

2. EXPERIMENTAL

Ironstone ore was supplied in the form of crushed and lumpy ores. They have different appearance (figure 1) and chemical compositions. XRF analysis of ironstone ores is given in table 1. The ores were further crushed and then grinded using ring mill and then sieved into different particle size range. The size range used in this investigation was 106-200 μm.

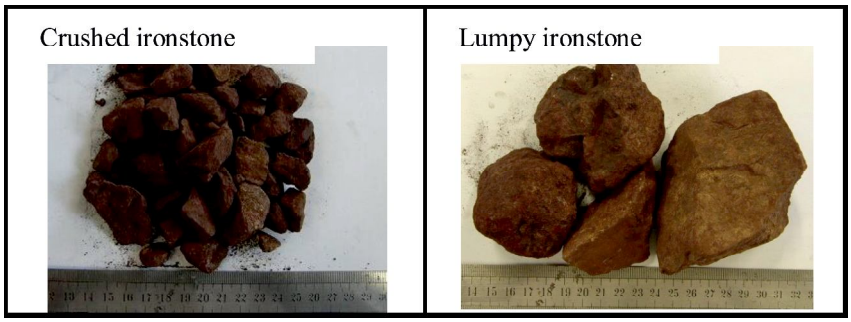

Figure 1: Photo of raw ironstone ores

Table 1: Chemical composition of ironstone ores

Ore	Chemical composition, wt%					
	Fe_2O_3	SiO_2	Al_2O_3	Mn_3O_4	K_2O	MgO
Crushed ironstone ore	40.6	44.3	4.21	1.30	0.81	0.46
Lumpy ironstone ore	21.4	68.9	3.20	0.63	1.01	0.35

A vertical tube furnace with a programmable temperature controller was used to heat the sample up to the targeted temperature. The sample temperature was measured with a Type B thermocouple. The reactor was made from recrystallized high purity alumina inner and outer tubes which provided controlled gas flow. The flow rate of the inlet gas introduced into the reactor was controlled by mass flow controller (5850E Brooks Instruments). Experimental set up is presented elsewhere [10].

About 0.7 gram of the ore was placed in an alumina or graphite crucible which was suspended 5 mm below the tip of the alumina inner tube, which was inserted into the outer tube from the top. Changes in ironstone ores upon heating were examined in air, argon and CO gas atmosphere. In experiments with carbon monoxide, the reactor was flushed with argon at a flow rate of 1L/min at

room temperature for 10 minutes before it was moved down to the hot zone of the furnace. Once the sample temperture reached the targeted temperature, argon was switched off and CO with flow rate 0.5 L/min was switched on.

Samples before and after experiments were analysed by XRD and SEM/EDS. XRD analysis was carried out using X-ray diffractometer (45KW, 40 mA), with step scans from 20 to 90°, a step interval of 0.02 degree and 58 s count time per step. The XRD patterns were analysed qualitatively using X'PertHighScore Plus software. SEM analysis was done using a Hitachi S-3400 SEM fitted with an Oxford Isis energy dispersive X-ray analyser (EDS) which enabled a quantitative and semi quantitative chemical analysis at different points and areas within the sample. Samples for electron microscope analysis were prepared by hot mounting in bakelite resin mounts, using struers mounting press. The mounted specimens were then polished on grinding papers followed by polishing on 3 μm and 1 μm diamond pads. Finally samples were coated with carbon.

The oxygen content of the reduced samples was determined using a LECO TC-600 Oxygen analyser (LECO Corporation, St. Joseph, USA) based on a basic combustion method. A sample (approximately 0.5 g) was loaded into a high-purity graphite crucible and fused at temperatures up to 3000°C in an inert gas. The oxygen in the sample reacted with carbon forming carbon monoxide. Oxygen content in the form of CO or CO_2 was measured using infrared detection. A reference material for calibration was tungsten oxide which is used for high level of oxygen in a sample (up to 20.5 wt%).

3. EXPERIMENTAL RESULTS

3.1. Calcination in Air

Calcination of ironstone ores in air was done at 1100°C in a muffle furnace. Heating and cooling rate was 5 °C/min. In these experiments, alumina crucibles were used; the sample holding time at 1100°C was 3 hours. The weight loss as a result of moisture and chemically-bonded water removal, and decomposition of carbonates was 5.2% and 2.4% for crushed and lumpy ironstone ores, respectively. Major phases identified by the XRD analysis were quartz and hematite.

3.2. Calcination in Argon

The behavior of crushed and lumpy ores upon heating in argon was studied using graphite and alumina crucibles in the temperature range 800-1150°C for 30 minutes.The weight loss measured upon heating in argon is presented in table 2.

Table 2: Weight loss (%) of ironstone ores upon heating in argon

Ore		Temperature, °C			
		800	1000	1100	1150
Crushed ironstone ore	Graphite crucible	4.9	6.48	7.4	8.6
	Alumina crucible	4.9	5.44	6.04	6.33
Lumpy ironstone ore	Graphite crucible	2.1	2.91	3.8	4.2
	Alumina crucible	2.1	2.37	2.45	2.62

The weight loss of lumpy ore in an alumina crucible changed only slightly with the calcination temperature, and was close to the weight loss in calcination at 1150°C in air (2.4%). A change in the weight loss of the crushed ore in an alumina crucibble with temperature also was not

high, although more significant than for the lumpy ore. The weight loss of ores calcined at 1000-1150°C in graphite crucibles was higher than that in alumina crucibles, indicating that graphite reacted with the ore, although a fractitonal oxidation of graphite by the small level of oxygen entered the reactor with argon cannot be excluded.

XRD spectra of original crushed ore and samples heated to different temperature in argon in graphite crucibles are presented in figure 2. XRD analysis of lumpy ore gave similar results. Hematite in both crushed and lumpy ores was reduced to magnetite. Reduction of hematite to magnetite was incomplete at 800°C and 1000°C, while no hematite peaks were observed in the XRD spectra of crushed and lumpy ores calcined in argon at 1100°C and 1150°C. A sample of crushed ore calcined at 1150°C in argon contained fayalite which was not detected in the lumpy ore calcined under the same conditions.

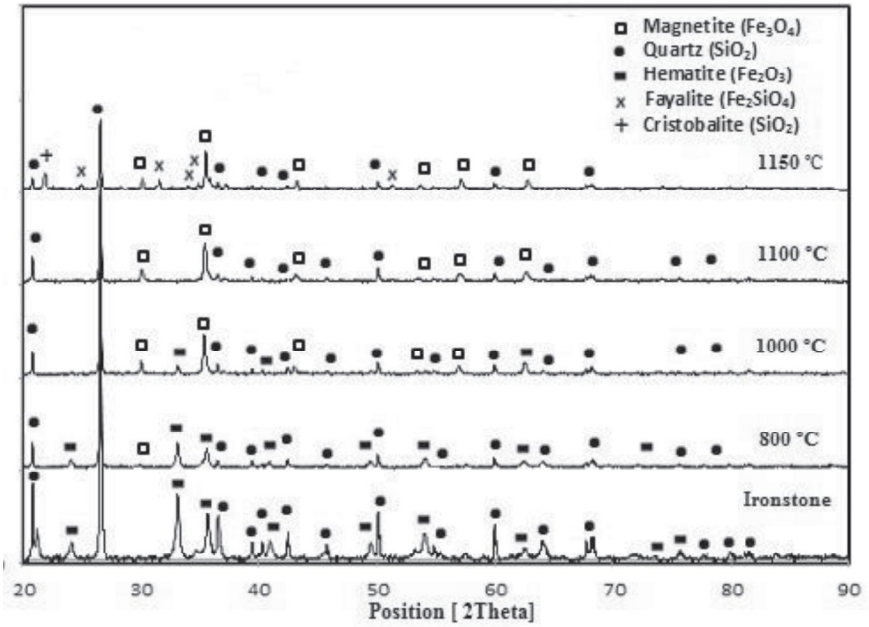

Figure 2: XRD pattern of crushed ironstone calcined in Ar in a graphite crucible

3.3. Reduction of Ironstone Ores by CO

Reduction of ironstone ores by CO was studied in the temperature range of 1000-1150°C in alumina crucibles, and 800-1150°C in graphite crucibles. The weight loss of ironstone ores in 30-min experiments in alumina crucibles is presented in table 3.

Table 3: Weight loss (%) of ironstone ores reduced by CO in alumina crucibles

Ore	Temperature, °C		
	1000	1100	1150
Crushed ironstone ore	15.4	13.8	8.5
Lumpy ironstone ore	7.8	7.8	5.2

The weight loss of crushed ore decreased with increasing temperature from 1000°C to 1150°C. The weight loss of lumpy ore was the same in experiments at 1000°C and 1100°C but and decreased with increasing temperature from 1100 to 1150°C.

Reduction experiments in graphite crucibles at temperatures of 800, 1000, 1100 and 1150°C

were carried out with different reaction time up to 40 minutes. The weight loss versus time at different temperatures is plotted in figure 3 for crushed ore and in figure 4 for lumpy ore. The weight loss of samples contained in a graphite crucible was higher than that recorded in an alumina crucible, although the difference was not significant. The weight loss of crushed ore in experiments at 800°C and 1000°C was about the same and decreased with increasing reduction temperature from 1000 to 1150°C as in experiments in alumina crucibles.

The weight loss of lumpy ore slightly increased with temperature in the temperature interval 800-1100°C and decreased when temperature increased further to 1150°C.

Figures 3 and 4 also show a theoretical weight loss calculated from the conversion of Fe_2O_3 to Fe_3O_4, FeO and Fe. In the theoretical weight loss calculation, the weight loss due to removal of chemically-bonded water and decomposition of carbonates was taken into account.

The oxygen content of reduced samples was determined using LECO analysis. Extent of reduction was then calculated based on the oxygen left in a sample measured by LECO analysis and total oxygen associated with iron oxide. The results are presented in table 4.

The extent of reduction of crushed ore dropped when temperature increased from 1000 to 1100°C and dropped significantly with further increase in temperature to 1150°C. The extent of reduction of lumpy ore also strongly decreased when temperature was increased from 1100°C to 1150°C. The extent of reduction of ores calculated using data from the LECO analysis correlates well with the weight loss of samples.

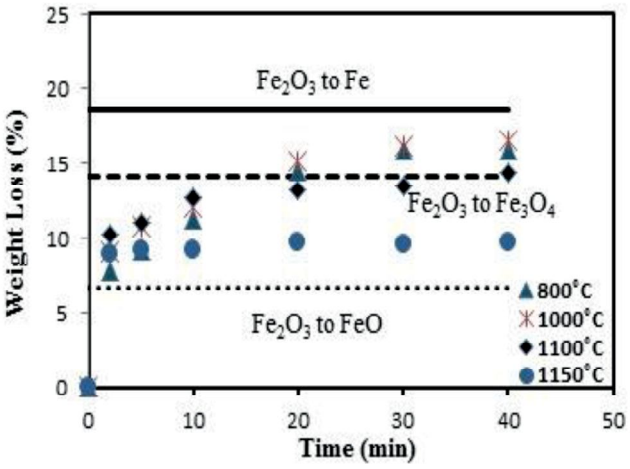

Figure 3: Weight losses of the crushed ironstone ore in CO

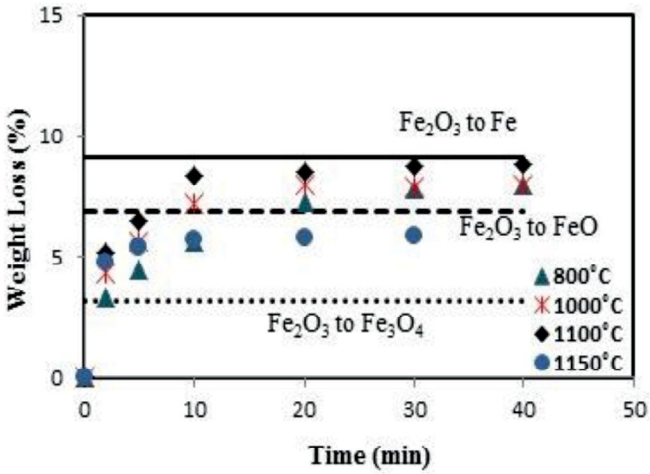

Figure 4: Weight losses of the lumpy ironstone ore in CO

Table 4: Extent of reduction of ironstone ores in CO in graphite crucibles (%)

Ore	Temperature, °C			
	800	1000	1100	1150
Crushed ironstone ore	79.1	82.4	68.8	33.1
Lumpy ironstone ore	78.1	79.5	82.7	47.2

3.4. Analysis of Reduced Samples

Samples of ironstone ores after reduction were subjected to XRD and SEM/EDS analyses. XRD spectra of crushed ironstone reduced at 800°C are shown in figure 5. Hematite was quickly

reduced to magnetite and further to wustite; no hematite peaks were observed in the XRD spectrum after 2 min reaction; magnetite peaks were not seen in the XRD pattern of the sample after 5 min reaction. 10-min reduction resulted in formation of metallic iron and fayalite. Wustite was observed in the sample reduced for 10 min but was not seen in the sample after 20-min reaction. XRD spectra of crushed ironstone reduced at 800°C for 20-40 min contained peaks of metallic iron, fayalite and quartz.

XRD spectra of samples of crushed ironstone reduced at 1000-1100°C for different times were similar to those for the sample reduced at 800°C. Fayalite phase was detected at the earlier stage, after 2 min reaction, while peaks for metallic iron in the sample reduced at 1100°C appeared only after 20-min reaction. Weak crystobalite peaks were seen in the XRD spectrum of a sample after 30-min reduction at 1100°C.

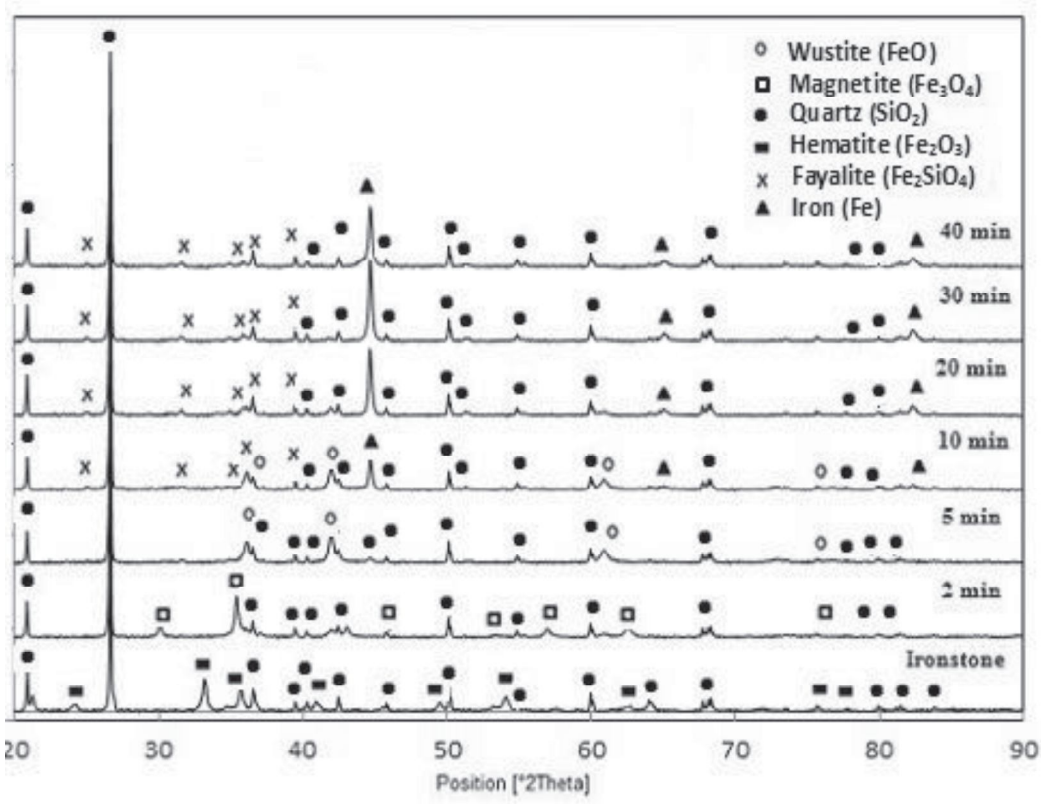

Figure 5: XRD spectra of crushed ironstone ore reduced by CO at 800°C

XRD analysis of crushed ore subject to up to 30-min reduction at 1150°C did not detect metallic iron (figure 6). XRD spectra did not exhibit wustite peaks either. Phases detected in the crushed ironstone ore reduced by CO at 1150°C for 2-30 min, included magnetite, fayalite, quartz and cristobalite. Fayalite peaks became stronger while magnetite peaks weaker as reaction progressed.

A similar phase development was observed in the course of reduction of lumpy ironstone ore by CO. The main difference in the XRD spectra of crushed and lumpy ironstone ores was observed for samples reduced at 1150°C. XRD spectra of lumpy ore (figure 7) reduced at this temperature for 2-30 minutes did not include iron oxide peaks, but only fayalite, quartz and cristobalite.

However, SEM/EDS analysis detected wustite and metallic iron in lumpy ironstone ore reduced at 1150°C, which were not seen in the XRD spectra.

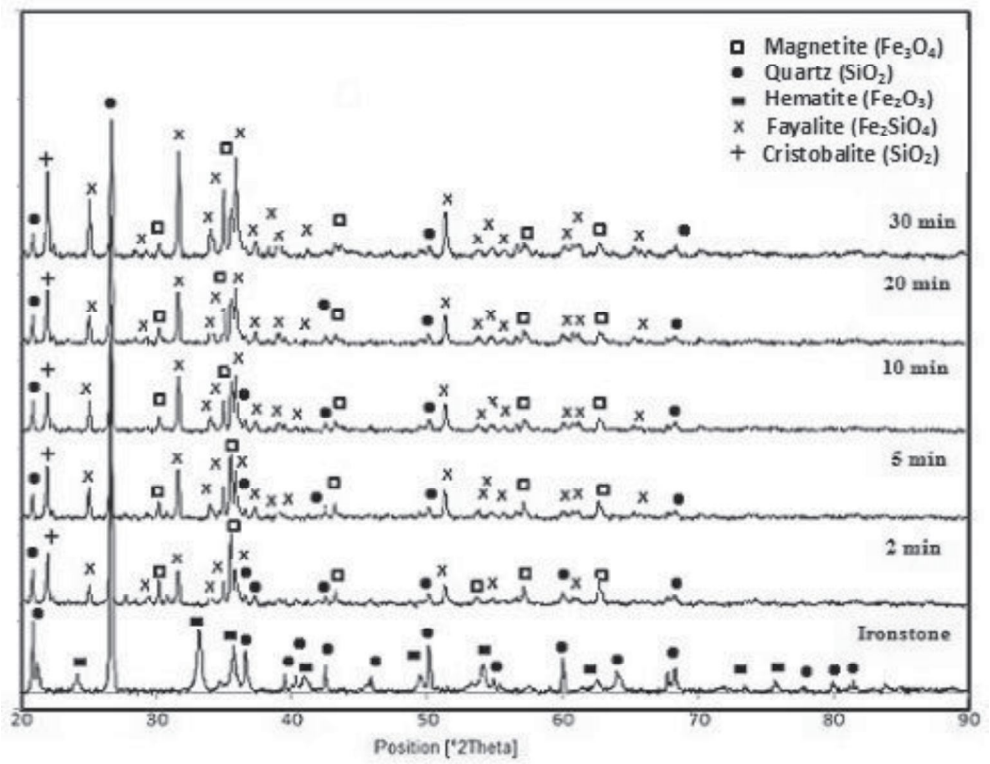

Figure 6: XRD spectra of the crushed ironstone ore reduced by CO at 1150°C

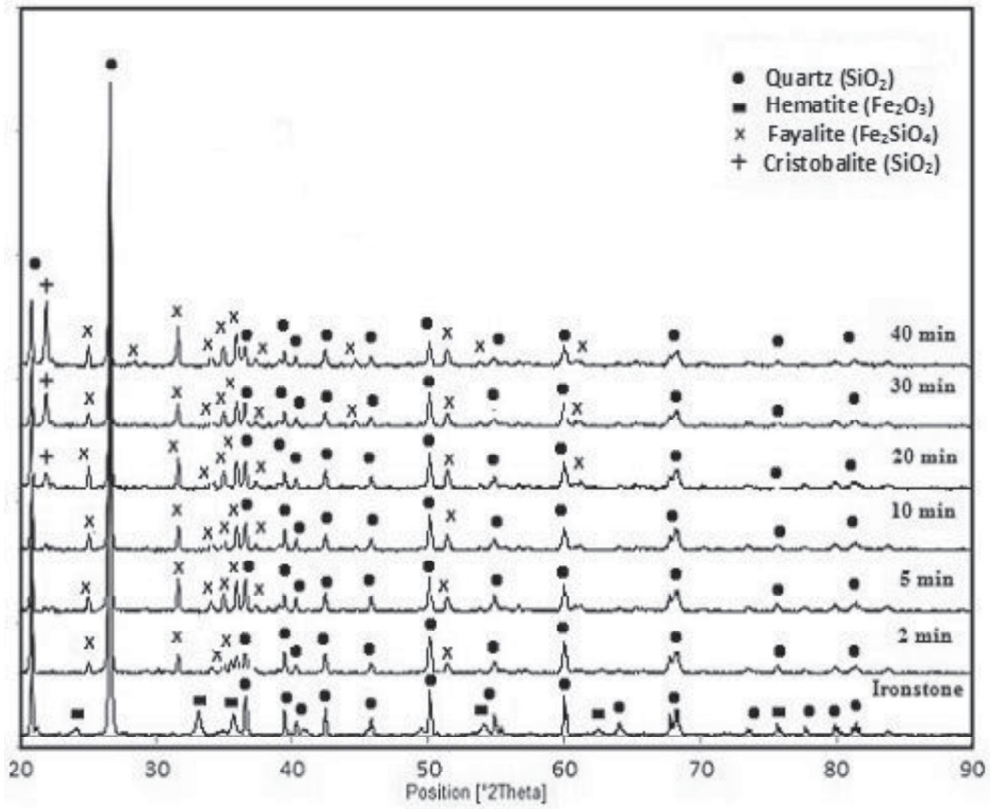

Figure 7: XRD spectra of lumpy ironstone ore reduced by CO at 1150°C

4. DISCUSSION

Main components of ironstone ores examined in this paper were quartz and hematite. Formation of fayalite from hematite and quartz can be presented by the following reaction:

$$Fe_2O_3 + SiO_2 = Fe_2SiO_4 + 1/2O_2 \qquad \Delta G^0 = 1683367 - 405T \text{ (J) [11]} \qquad (1)$$

Equilibrium oxygen partial pressure for this reaction is $2.22x10^{-15}$atm at 800°C, $2.25x10^{-8}$atm at 1100°C and $9.61x10^{-8}$atm at 1150°C.

A small amount of fayalite was detected by XRD analysis in a sample of crushed ironstone ore heated in argon to 1150°C. Upon heating in argon, hematite was decomposed/reduced to magnetite; which was a major iron-containing phase in both ores.

Reduction of fayalite by reaction (2) requires lower oxygen partial pressure: $6.24x10^{-21}$atm at 800°C, $7.91x10^{-15}$atm at 1100°C and $4.61x10^{-14}$atm at 1150°C; it is not feasible in heating of fayalite in argon, but can be expected in reduction by CO.

$$Fe_2SiO_4 = Fe + SiO_2 + 1/2O_2 \qquad \Delta G^0 = 870025 - 154.T \text{ (J)} \quad [11] \qquad (2)$$

SEM/EDS analysis of samples after reduction at 1100-1150°C showed that iron oxide particles were surrounded by molten slag, which restricted an access of CO to the reaction interface. Formation of liquid slag significantly decreased specific surface area. A dramatic decrease in specific surface area of both ironstone ores can be seen in table 5, which presents results of BET analysis of the specific surface area of samples reduced by CO at 1100 and 1150°C. When reduction temperature increased from 1100°C to 1150°C, the extents of reduction decreased from 69% to 33% for crushed ironstone ore and from 83% to 47% for lumpy ore (table 4). Metallic iron in both ironstone ores reduced at 1150°C was below the XRD detectable level, although it was observed in SEM/EDS analysis.

Table 5: Specific surface area of ores (m^2/g)

Ore	Before reduct.	1100°C, 5 min	1100°C, 30 min	1150°C, 10 min	1150°C, 30 min
Crushed ore	19.6	0.43	0.55	0.34	0.39
Lumpy ore	7.62	0.49	0.49	0.36	0.37

5. CONCLUSIONS

Chemical and phase composition of ironstones (crushed and lumpy) and reduction of ores by carbon monoxide were investigated in the temperature range 800–1150°C. Major phases in original ironstone ores were hematite and quartz. Upon heating of ores in argon, hematite was decomposed/ reduced to magnetite; traces of fayalite were detected in the XRD spectrum of crushed ironstone calcined in argon at 1150°C. Two major reactions observed upon heating of ores in CO were partial reduction of iron oxides and formation of fayalite. Degree of iron oxide reduction decreased with increasing temperature from 1100 to 1150°C for crushed ore, and in the range 1000-1150°C for lumpy ore. The degree of iron oxide reduction in the crushed ore was 82.4% at 1000 °C, 68.8% at 1100 °C and 33.1% at 1150 °C; reduction of iron oxide in lumpy ore reached 79.5% at 1000 °C, 82.7% at 1100 °C and 47.2% at 1150 °C.

Formation of liquid slag significantly decreased specific surface area with detrimental effect on reduction rate of iron oxides.

6. ACKNOWLEDGEMENT

This project was financially supported by Tasmanian Electrometallurgical Company and Australian Research Council (ARC Linkage Project LP120100672).

7. REFERENCES

[1] Nicolle, R., Rist, A., Mechanism of whisker growth in the reduction of wustite, Metallurgical Transactions B, 1979, 10B (3), p.429-438.

[2] Wagner, C., Mechanism of the reduction of oxides and sulfides to metals, Journal of Metals, 1952, 4 (Trans.), p.214-216.

[3] St John, D. H., Matthew, S.P., Hayes, P.C., The breakdown of dense iron layers on wustite in CO/CO_2 and H_2/H_2O systems, Metallurgical Transactions B, 1984, 15B(4), p.701-708.

[4] St John, D. H., Matthew, S.P., Hayes, P.C. Establishment of product morphology during the initial stages of wustite reduction, Metallurgical Transactions B, 1984, 15B(4), p.709-717.

[5] St John, D. H., Matthew, S.P., Hayes, P.C., Microstructural features produced by the reduction of wustite in H_2/H_2O gas-mixtures, Metallurgical Transactions B, 1982, 13B(1), p.117-124.

[6] Jozwiak, W.K., Kaczmarek, E.K., Maniecki, T.P., Ignaczak, W., Maniukiewicz W., Reduction behavior of iron oxides in hydrogen and carbon monoxide atmosphere, Applied Catalysis A: General, 2007, 326 (1), p.17-27.

[7] Turkdogan, E. T., Vinters, J. V., Reducibility of iron ore pellets and effect of additions, Canadian Metallurgical Quarterly, 1973, p.12, 9-21.

[8] Nigro, J. C; Tiemann, T. D., Prasky, Ch., Kinetics of CO reduction of hematite to magnetite and the effect of silica, PhD thesis, 1970, University of Wisconsin, USA.

[9] El-Geassy, A. A; Nasr, M. L., Influence of manganese oxide and silica on the morphological structure of hematite compacts, Steel Research Institute, 2010, 3 (81), p.178-185.

[10] Turkdogan, E. T., Physical Chemistry of High Temperature Technology, New York, Academic Press, 1980.