

Thermal investigations of direct iron ore reduction with coal

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Abstract

In this paper, fundamental mechanisms for iron ore reduction in coal–ore mixtures have been investigated using several advanced experimental techniques. Firstly, the thermal properties of coal–ore mixtures were studied and apparent specific heat of coal–ore mixtures against temperature was obtained at a heating rate of 10 °C/min. Several exothermic and endothermic peaks were observed which were related to the decomposition reactions and reduction. The flue gases from the mixture were analysed using a mass spectrometer. Secondly, the X-ray diffraction (XRD) and the iron phase analytical techniques were applied to identify the iron phase changes with the temperature. It has been found that coal devolatilisation and iron oxides reduction occur simultaneously during the heating of the mixture. H₂ and CO gases produced from coal devolatilisation and char gasification were responsible for the reduction of iron oxides at these temperatures. Iron oxides undergo step-wise reduction over the whole process. The results in this work provide a fundamental understanding for the direct reduced ironmaking processes. © 2003 Elsevier B.V. All rights reserved.

Keywords: Coal; Iron ore reduction; Direct reduced iron; Thermal property

1. Introduction

Substantial developments in direct reduction ironmaking (DRI) technologies have been recently conducted providing sustainable mean, for metallurgical operations. The largest advantage of the DRI technologies relies on the fact that DRI does not require cokemaking and sintering. Both cokemaking and sintering, being at the front end of the conventional blast furnace ironmaking technology, are considered as costly for the new process construction and are consistently causing environmental concerns. The DRI process, on the other hand, consists of carbothermic reduction of iron oxide directly with the volatiles liberated during coal devolatilisation as well as the carbon monoxide regenerated from coal char. This process provides an advanced utilisation opportunity for the high volatile coals, which were otherwise unusable in the steel industry.

There has been extensive work performed on iron ore reduction of coal–ore mixtures and its kinetics [1–20]. Opti-

misation of the DRI process, however, requires knowledge of the thermal properties of the coal–ore mixtures and mechanism of the reduction reactions, which have still not been well understood. It is therefore necessary to have an insight into fundamental mechanisms for these complex reactions. The aim of this work is to investigate coal–ore reactions of their mixtures during heating, using several advanced measuring techniques. Thermal property, gas analysis, and iron phase changes during heating of the mixtures were obtained, through which fundamental insights into coal and iron ore behaviour and their interactions are provided.

2. Experimental

Coal C1 and iron ore O1 both from Australian origin were used in this work. The coal has 33.5% volatile matter and 6.5% ash in air-dry base, and has 85.1% C, 5.5% H, 2.1% N, 0.7% S and 6.6% O in daf base. The major components of the iron ore are 62.1% Fe, 4.33% SiO₂ and 1.98% Al₂O₃. Both samples were dried under vacuum at 80 °C for 2 h before proceeding with experiments. The mean particle size of coal and iron ore was –80 and –50 μm, respectively.

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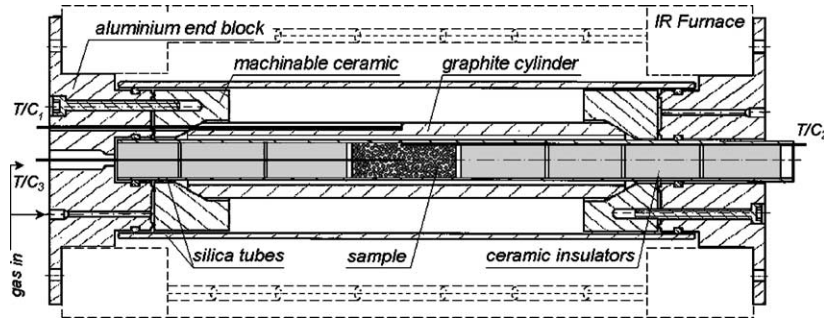


Fig. 1. The cross-sectional diagram of the instrument used for thermal property measurements.

A mixture of coal and iron ore particles at a mass ratio of 20:80 was used throughout the study.

Several measuring techniques were used for investigating the reactions between coal and ore in the study. The thermal property measurements were performed using the computer aided thermal analysis technique [21,22], with the instrument shown in Fig. 1. This method provides an opportunity for dynamic thermal analysis by heating the sample with controlled heat flux while continuously monitoring boundary temperature conditions within the sample. The heat transfer is, then, calculated using inverse numerical modelling technique. There was a substantial effort in the past [21–27] to apply inverse methods in a variety of different thermal studies. It was shown that, with controlled heating conditions it is possible to obtain accurate thermal characterisation of the materials.

In this work, the sample with 30 mm in length and 10.6 mm in diameter was packed in a silica glass tube to the density of 1860 kg/m^3 , and heated by radiation from a surrounding graphite cylinder. The heating rate of the furnace was typically maintained at 10°C/min , controlled through a type K thermocouple embedded in the graphite. The sample was maintained under inert atmosphere with an argon flow of 5 ml/min through the glass sample tube. Sample temperatures were continuously measured by thermocouples positioned at the surface and in the centre of the sample. The measured data were acquired at a frequency of 1 Hz, and the typical temperatures for one experimental run for coal–ore mixture in a ratio of 20:80 are shown in Fig. 2. The heat flux at the surface of the sample was calculated by assuming heat transfer from the graphite heating element to the sample was performed predominantly by radiation and was estimated using Eq. (1). For this purpose and to ensure uniform emissivity of the glass, the outside surface of the sample glass tube was coated with a thin layer of carbon soot, prior to positioning the sample tube centrally to the graphite heating cylinder.

$$Q = F_{1-2}\sigma(T_g^4 - T_s^4) \quad (1)$$

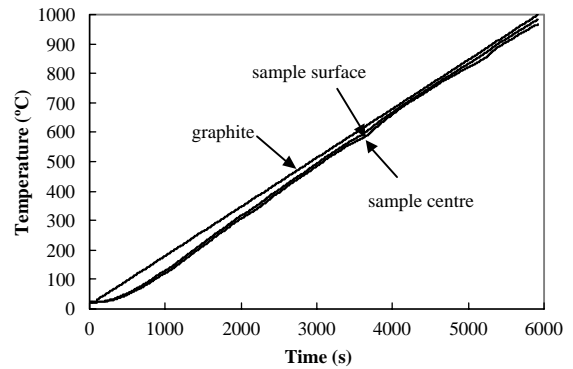


Fig. 2. Time–temperature history during heating of coal–ore mixture at a mass ratio of 20:80 and heating rate of 10°C/min .

where Q is the heat flux (W/m^2), F_{1-2} the radiation shape factor, σ the Stefan–Boltzmann constant ($5.67 \times 10^{-8} \text{ W/m}^2 \text{ K}^4$), and T_g and T_s are the temperatures of the graphite and the surface of the sample (K), respectively.

The one-dimensional heat conduction in the sample is given by the following expression:

$$\rho C_p \frac{\partial T}{\partial t} = k \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) \quad (2)$$

where ρ is the density (kg/m^3), C_p the specific heat (J/kg K), k the thermal conductivity (W/m K), T the temperature (K), t the time (s) and r the radius (m).

The sample was numerically divided into a number of nodes (n) across the radius. For each node an estimate was made based on the heat balance principle (i.e. heat accumulated in the node equals to the difference between the incoming and outgoing thermal energies). The boundary conditions of the system were the temperatures measured at the centre and surface of the sample, and the heat flux calculated according to Eq. (1). A computational matrix was then generated using Eq. (3) to estimate the volumetric specific heat based on the initial mass of the heated sample. For closer familiarising with the equation evaluation procedure the reader is referred to [21–24].

$$\rho C_p = \frac{2\pi n \Delta x Q(t)}{(\Delta x^2 \pi / 4 \Delta t)(T_0^t - T_0^{t-1}) + (\Delta x^2 \pi / \Delta t)(n - (1/4))(T_n^t - T_n^{t-1}) + \sum_{i=1}^{n-1} (2\pi \Delta x^2 i / \Delta t)(T_i^t - T_i^{t-1})} \quad (3)$$

where ρC_p is the volumetric specific heat ($\text{J/m}^3 \text{K}$), n the number of nodes, T_i^t the temperature expressed in K of the node i for the time t (s) and $Q_{(t)}$ the heat flux expressed in W/m^2 for time t .

The volumetric specific heat in this case is apparent, which means that it includes heats developed due to decomposition, transformation and reaction. If, for instance, endothermic heat is developed in the sample, it results in increase of the apparent specific heat, hence the heat is consumed by the sample. On the contrary, if an exothermic reaction is developed during heating, the apparent specific heat will show decrease of its values. The performance of the above-mentioned measurement method was tested previously [22] on a range of different materials and accuracy of approximately $\pm 2\%$ was found in the measurement data. Maximum temperature was limited to 1000°C , which was the maximum limit of the furnace used. Results are normally plotted against average of the two sample temperatures.

Thermal studies of direct iron ore reduction were, in this work, incorporated with analysis of the gaseous products using a mass spectrometer Prima 600 connected to the gas outlet of the apparatus described above. Argon gas was flown at a rate of 100 ml/min across the sample for the purpose of these measurements. The water vapour and larger molecular weight volatiles generated during heating of the samples were condensed at the outlet of the furnace prior to the gas analyser. The volume percentages of gases as a function of sample temperature were then obtained. The coal–ore samples, which were heated up to certain temperatures in the above furnace, were further collected and analysed using an X-ray diffraction (XRD), and an iron phase analysing technique. The XRD uses the “fingerprint” of a crystalline material to allow identification of unknown phases in a mixture. Rapid identification of unknown phases can be possible using search/match software available at the unit. The samples were also sent to chemical laboratory for carbon and iron phase analysis.

3. Results

3.1. Apparent specific heat

The apparent specific heats for single coal C1 and iron ore O1 were measured at a heating rate of 10°C/min under Ar atmosphere, as shown in Fig. 3. Coking coal C1 exhibits a rapid and significant exothermic reaction occurring between 420 and 460°C , which is thought to be caused by both physical and chemical related changes in the coal plastic region, i.e. tar formation, tar vaporisation and resolidification. Following the tar formation, the secondary devolatilisation and hydrogen release occurred over a temperature range of 500 – 1000°C . Previous work [28] has shown that the evolution of CO for C1 initiated at 450°C and completed at about 950°C , with a maximum evolution rate at 720°C , whereas H_2 started from 495°C and contin-

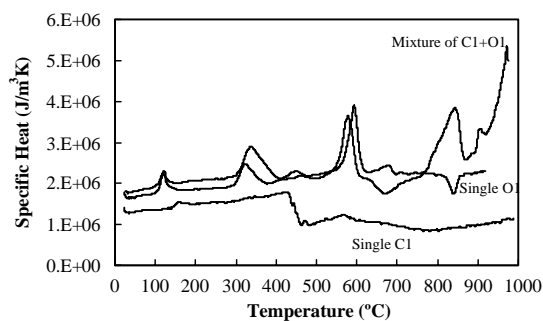


Fig. 3. Specific heats of single coal C1, single ore O1, and their mixture at 20:80 mass ratio.

ued to evolve at 1000°C , with a maximum rate at 785°C . The specific heat of O1 iron ore was also measured, which exhibited several sharp peaks. The first peak at 120°C represents the endothermic water vaporisation, and the second at 340°C was caused by dehydroxylation of goethite ($\text{FeO}(\text{OH})$, hydrated iron oxide) with formation of hematite (Fe_2O_3). The third endothermic peak at around 600°C was due to breakdown of kaolinite ($\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_8$) [29]. The fourth peak, caused by magnetic transformation of Fe_2O_3 [30], appeared at 685°C , whereas the exothermic trough at 843°C was most likely caused by the partial reduction of hematite from the carbon present in the ore.

The specific heat of the mixture at a mass ratio of 20:80 exhibits similarities with the pure iron ore, prior to 600°C . Dehydroxylation and decomposition of kaolinite are the dominant reactions for the mixture, with peaks being similar to those of single iron ore. Primary coal devolatilisation has initiated below 600°C as shown for single C1 coal, however the rate is reduced at the presence of iron oxides [3,4]. Above 600°C , the curve was substantially different from that of either the single iron ore or coal. An exothermic reaction occurred at around 690°C , followed by two strong endothermic reactions. These reactions are most likely due to the iron ore step-wise reduction, i.e. the reduction of hematite (Fe_2O_3), magnetite (Fe_3O_4) and wustite (FeO), respectively.

Fig. 4 shows the specific heats of iron ore reduction of mixtures of C1–O1 and coke–O1 at a mass ratio of

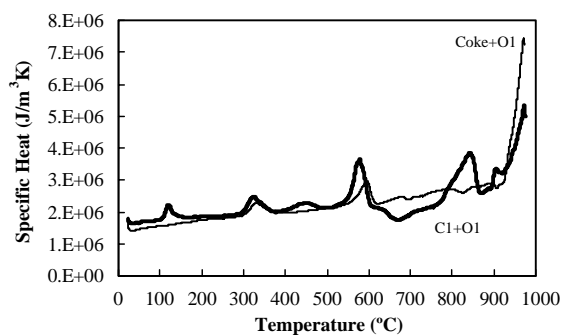


Fig. 4. Specific heats of mixtures of C1–O1 and coke–O1 at a 20:80 mass ratio.

20:80. Similar to that of C1–O1 mixture, the specific heat of coke–O1 mixture only exhibits two endothermic peaks at 340 and 595 °C, respectively. These reactions are of the same origin as the dehydroxylation and decomposition reactions of the pure iron ore in the same temperature range. The intensity of the peak at 595 °C in coke–O1 is smaller than C1–O1 mixture. The reason is that the peak for the latter is a sum of the endothermic reactions of iron ore decomposition and the secondary devolatilisation of coal.

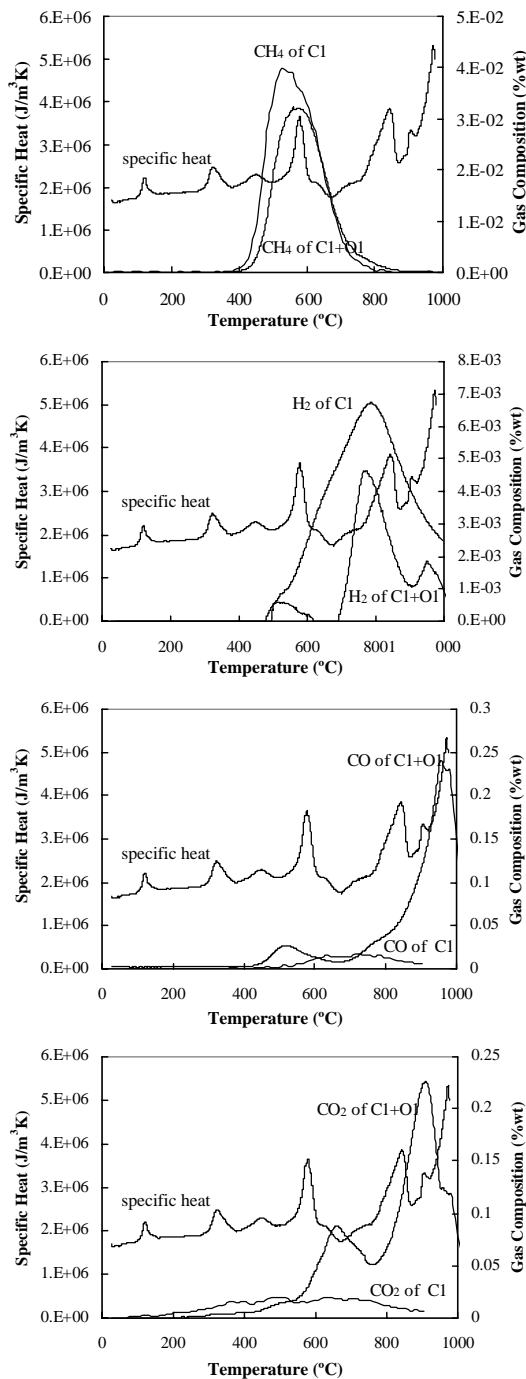


Fig. 5. Mass spectrometric analysis of gas evolution of C1 + O1 mixture during heating.

Unlike that of C1–O1 mixture, at higher temperatures no significant peaks were observed for coke–O1 mixture until the sample reached 920 °C. At temperatures above 920 °C, similar to the C1–O1, a rapid increase of specific heat was observed for coke–O1 mixture, due to char gasification with CO₂.

The above observation suggests that CO and H₂ volatiles generated from coal decomposition are the predominant reductants for iron oxides at lower temperatures, whereas the iron ore reduction by char gasification dominates above 920 °C.

3.2. Product gas analysis

The gas analysis was performed by connecting a mass spectrometer to the outlet of the heating furnace. Fig. 5 shows the weight percentages of product gases CH₄, H₂, CO and CO₂ of the coal–ore mixture as a function of temperature, in comparison with the specific heat. The CH₄ was predominantly produced from coal devolatilisation, and released between 450 and 800 °C, with a maximum value at 600 °C. The H₂ started to release at 500 °C, and the concentration decreased with increasing the temperature from 530 °C, and disappeared from 600 to 700 °C, which indicated a great consumption of H₂ gas due to the significant

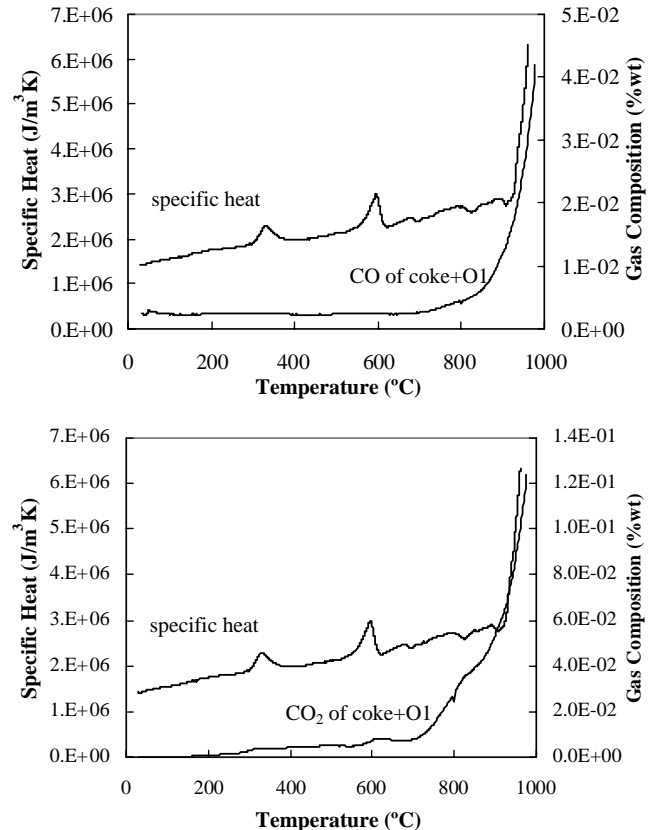


Fig. 6. Mass spectrometric analysis of gas evolution of coke + O1 mixture during heating.

reduction of the iron oxide. The H_2 increased again from 700 °C, reaching a peak at 780 °C, and decreased again. Compared to the single coal C1, the H_2 concentration of C1–O1 mixture is much lower due to the consumption of H_2 as a reductant gas for iron oxides, with the peak temperature similar to each other, as shown in Fig. 5. The CO started to release through by the coal devolatilisation at 450 °C, and decreased with the temperature again from 530 to 700 °C, which was due to the consumption by reduction. The CO concentration increased rapidly from 700 °C, followed by a decrease at about 950 °C. The CO_2 concentration exhibited an inverse trend of CO below 780 °C which was pro-

duced from iron ore reduction by CO predominantly from volatile, and increased dramatically at temperatures above 780 °C, indicating the carbon gasification has become significant within this temperature range. Rapid increasing of both CO and CO_2 indicates that significant carbon consumption occurred due to gasification.

Fig. 6 shows the mass spectrometric analysis of coke and O1 mixture at the same mass ratio. The CO and CO_2 concentrations were extremely low and remained constant below 700 °C. They started to increase at 700 °C, and became rapid from 800 °C. It is more than likely that direct reduction of iron oxide by solid carbon occurred between 700 and

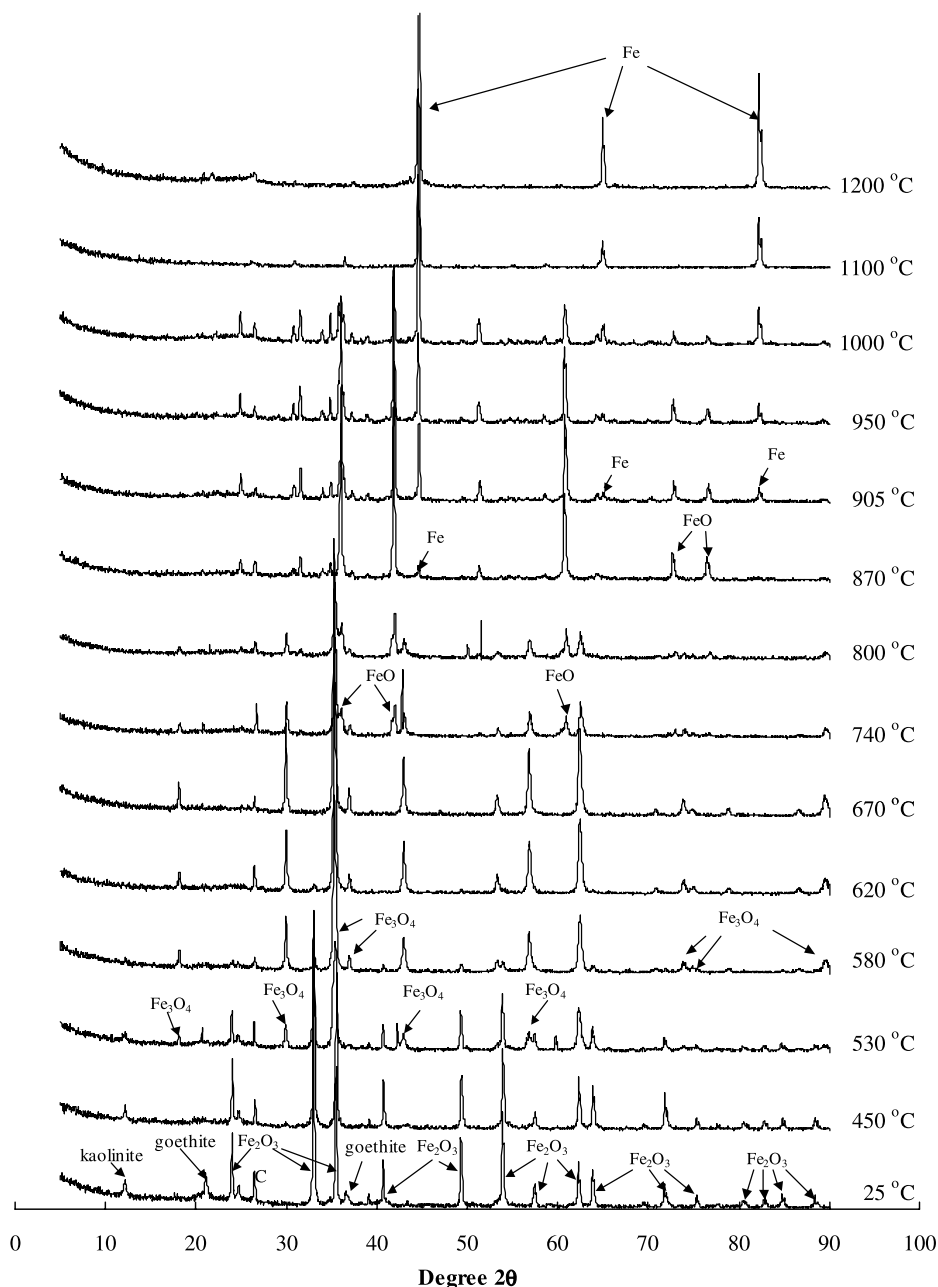


Fig. 7. X-ray diffraction analysis of mixture of C1 + O1 heated at different temperatures.

800 °C with the CO₂ as a primary product gas. Significant carbon gasification occurred at temperatures above 800 °C, and the reduction of iron oxide occurred through reducing gaseous phase, for example CO and H₂ produced from carbon gasification with CO₂ and H₂O, respectively.

3.3. XRD analysis

Coal and ore samples were prepared in a furnace at various temperatures followed by cooling with a rate of approximately $-100\text{ }^{\circ}\text{C}/\text{min}$, and were further analysed by XRD. Two of the samples heated at temperatures above 1000 °C were prepared separately in a muffle furnace. Fig. 7 shows the XRD analysis of coal–ore mixture made at different temperatures. At 25 °C (i.e. original coal and iron ore mixture), the sample was dominated by Fe₂O₃ and carbon, with minor phases of goethite (FeO(OH)) and kaolinite. At 450 °C, only the disappearance of goethite was evident, due to the dehydroxylation reaction at 340 °C as indicated by the specific heat. The first step reduction of Fe₂O₃ forming Fe₃O₄ was initiated below 530 °C, and completed at a temperature between 620 and 670 °C. The rate for the first step reduction within 530–580 °C was much higher than that within 580–670 °C. It was evident that the kaolinite disappeared between 580 and 620 °C, due to the thermal decomposition as found by the specific heat study presented above. The second step reduction of Fe₃O₄ to form FeO initiated between 670 and 740 °C, and completed below 870 °C. Rapid reduction rate was indicated between a temperature range of 800–870 °C. The third step reduction of FeO to form metallic Fe initiated from 870 °C. Small amount of metallic Fe was formed at 870 °C. At 1000 °C, the metallic Fe dominated the sample, with a minor phase of FeO. The 1100 and 1200 °C samples were primarily metallic Fe phase.

3.4. Iron phases analysis

Fig. 8 shows the quantitative iron phase and carbon content as a function of temperature. The analysis showed that the Fe³⁺ started to reduce at 450 °C the reduction was almost completed at 870 °C. The Fe²⁺ percentage increased from 450 °C, reaching maximum at 870 °C, and decreased with further increasing of the temperature up to 1100 °C. The metallic iron rapidly increased from 870 °C and reached up to 98.7% at 1200 °C, which is consistent with the XRD results. Also included in Fig. 8 is the carbon content of the sample as a function of temperature. The carbon was reduced from 17 to 14% as temperature increased from 25 to 800 °C. The rate of carbon release was slow, and was identical to the rate of coal devolatilisation. The carbon reduced rapidly at temperatures above 800 °C, which is demonstrated to be due to carbon gasification according to the analysis of coke and O1 mixture. The concentration of carbon in the reduced iron was found to be approximately 3.5%.

3.5. Scanning electron microscope (SEM) analysis

Fig. 9 shows the cross-sectional SEM images of iron ore particles in the coal–ore mixture made at different temperatures. The chemical analysis can be carried out through an energy dispersion system (EDS) with the SEM. In the sample prepared at 560 °C, it was evident that ore particles were heterogeneous, with mineral grain (deep gray area) included in the ore particles. The ore particle exhibited a dense phase, with some macropores randomly scattering throughout the particle. In the 670 °C sample, cracks were observed within the particle, indicating the thermal decomposition occurred below this temperature. From the specific heat and XRD analysis, it is obvious that the reduction of Fe₂O₃ has also occurred below this temperature. However, it is impossible

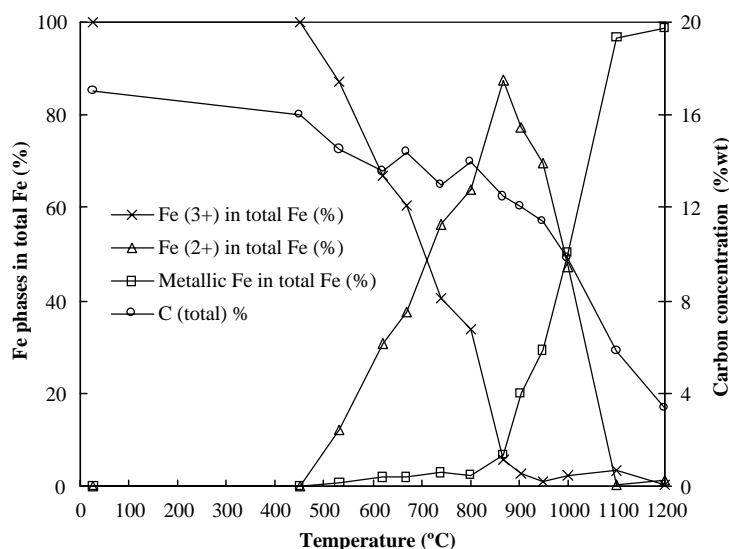


Fig. 8. Iron phases change and carbon content as a function of temperature.

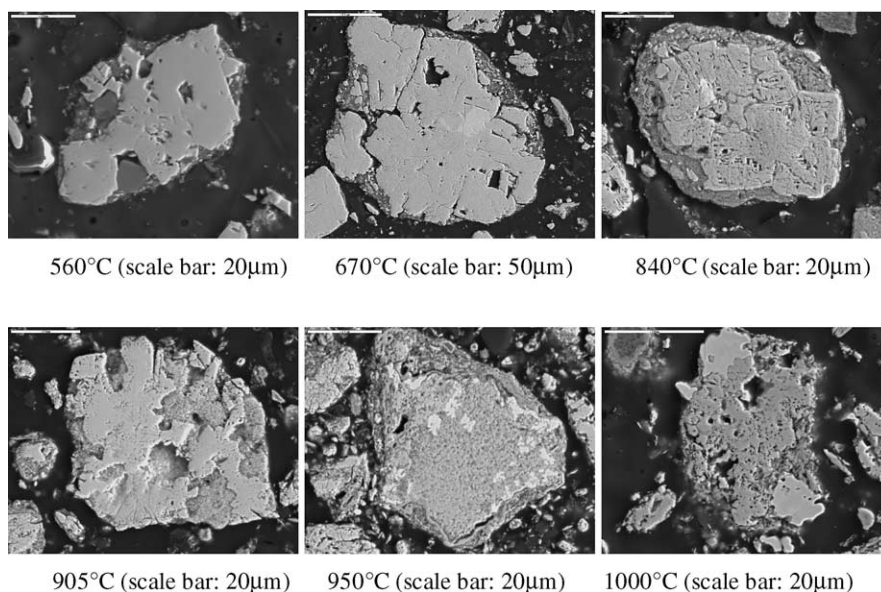


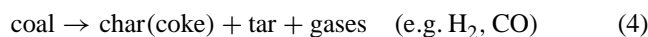
Fig. 9. Scanning electron microscopic (SEM) images of iron ore particles in coal-ore samples at different temperatures. Below each image is the temperature at which the sample was prepared, followed by the length of scale bar.

to detect the phases through the brightness of the area. The ore particle in sample heated to 840 °C exhibited a developed porous system due to the reduction reaction. Some bright area can be seen in the sample prepared at 950 °C, which was confirmed to be metallic iron through the EDS analysis. The bright spots were seen severely in the samples heated to 950 and 1000 °C.

4. Discussion

Several measuring techniques have been applied to characterise the coal-ore mixtures under 10 °C/min heating rates, providing consistent understanding of fundamental reactions during the reduction process. It can be concluded that coal and iron ore reactions are complex and are coupled extensively in the coal-ore mixture system. Furthermore, the changes in the reactions are heavily dependant on the heat transfer parameters including size, shape, sample density and heating rate. From here it is noteworthy mentioning that the results presented in this work depict reaction mechanism for the current heating conditions and parameters.

When heated, coal particles undergo severe devolatilisation producing solid coke, tar and light gases, as illustrated by the following reaction:



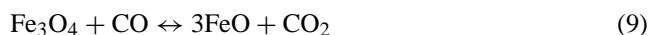
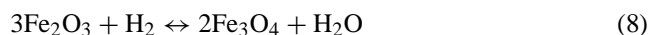
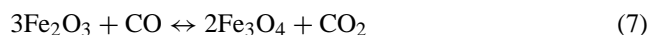
Coal goes through the primary devolatilisation between 420 and 460 °C, releasing tar, followed by secondary reactions at temperatures above with the release of light gases. CH₄ is released primarily between 450 and 700 °C, whereas H₂ and CO are released at higher temperatures becoming a reductant source for ore reduction.

Carbon gasification with CO₂ and H₂O occur at temperatures above 800 °C to produce CO and H₂ for iron oxides reduction, which are represented by the following reactions:



The CO₂ and H₂O source for gasification reactions is generated from the reduction of iron oxide by CO and H₂, respectively, which is detailed below.

Reduction of iron oxides in a direct reduction system has been known to occur by gaseous phases, for example CO and H₂, rather than the solid carbon [20]. It has been shown from the present study that the iron ore (Fe₂O₃) undergoes stepwise reductions by CO and H₂, which are represented by the following reactions:



The Fe₂O₃ reduction initiated below 580 °C, and has completed by 670 °C. The Fe₃O₄ was reduced between 670 and 870 °C to form FeO. The FeO was reduced thereafter by CO generated predominantly from carbon gasification. The reduction of iron oxides was almost completed by 1200 °C, resulting in formation of metallic iron. It has been found that the volatile in the coal plays an important role in iron ore reduction, providing reductant adequate for complete reduction of Fe₂O₃ and Fe₃O₄.

5. Conclusions

From the current work the following conclusions have been driven out:

- At 10 °C/min heating rate and under Ar atmosphere, 98.7% of Fe₂O₃ in the initial iron ore was reduced to metallic Fe at 1200 °C in the 20:80 mass ratio mixture of coal and iron ore.
- Fe₂O₃ was reduced to Fe₃O₄ between 500 and 670 °C by CO and H₂ as products of coal devolatilisation.
- Fe₃O₄ was reduced to FeO between 740 and 870 °C by H₂ and CO as products of coal devolatilisation and CO as a product of char gasification. Rate of reduction was lower between 740 and 800 °C and rapid between 800 and 870 °C.
- FeO was reduced to Fe between 870 and 1200 °C mainly by CO from char gasification. The rate of reduction was rapid between 950 and 1100 °C.

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