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TG/DTA Study on the Carbon Monoxide and Graphite Thermal Reduction of a High-Grade Iron Nickel Oxide Residue with the Presence of Siliceous Gangu

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Abstract

The reduction behavior of a leach residue containing hematite (Fe₂O₃), nickel ferrite (NiFe₂O₄) and a small amount of siliceous gangue was studied using thermogravimetric (TG) and differential thermal analysis (DTA) techniques. Carbon monoxide and graphite were used as reductants and a wide range of temperatures were covered. Both non-isothermal reduction (15 ºC/min) and isothermal reduction tests with continuous measurement of the CO and CO₂ evolution were performed to evaluate the temperature dependence of the reduction kinetics. In order to further elucidate the reduction mechanisms, the reduced products were subject to various analyses, i.e. SEM/EDS, XRD, and EPMA. Results show that the reduction rate increased with the increase of temperature when using CO as the reductant. Change of the rate-controlling mechanism from the gaseous diffusion in the pores of the sample bed to the diffusion in the metallic product layer was found to have taken place in the isothermal tests, resulting in the variation of apparent activation energies from 6.7 kJ/mol to 41.1 kJ/mol with the progress of reduction. The siliceous gangue melted at 1200 ºC, inhibiting the reduction of the oxides. Effective reduction by graphite only occurred above around 1000 ºC. Reduction of the molten silicate took place above 1200 ºC resulting in the formation of Fe-Ni-Si alloys.

Keywords: TGA; DTA; Reduction; Hematite; Nickel ferrite; Silicate

1. Introduction

An integrated pyro- and hydro-metallurgical approach to treat nickel concentrates through sulfation roasting followed by leaching, is being investigated [1, 2] as an alternative processing route with potential environmental benefits. In this process, the majority of the non-ferrous valuable metals are leached with water after sulfation roasting, leaving iron in the leach residue as oxides. However, approximately 20% of the nickel reports to the leach residue due to the inevitable formation of nickel ferrite (NiFe₂O₄) during sulfation roasting [3]. This leach residue, which is mainly composed of hematite (Fe₂O₃), nickel ferrite, and siliceous gangue, can be a high-grade source of Ni (10 wt%) and Fe (50 wt%) for the production of ferronickel alloy. As a result, the reduction of the Ni- and Fe-bearing leach residue to produce ferronickel alloy becomes an integral part of the sulfation roasting route and was studied.
Kinetic study on the reduction of this residue with hydrogen as the reductant has been conducted and reported elsewhere [3]. In this work, the feasibility of using carbon monoxide and graphite as reductants to reduce the leach residue and its reaction kinetics were studied by means of TGA and DTA. The heterogeneous reduction kinetics and mechanism could be affected by various factors, such as the reduction temperature [4], the gas composition [5], the particle size [6], the original structure [7], the size [8] and shape [9] of the oxides ore pellets, and the sintering conditions [10], etc. Structural changes during the reduction process has been investigated extensively [11] and they also imposes a significant impact on the reduction rate [12, 13]. The changes in porosity, specific surface area and the pore size distribution have been reported to strongly depend on the reduction temperature [12, 14].

Fig. 1 displays the stability diagram of iron oxides in CO/CO$_2$ atmosphere, as well as CO partial pressure in the CO-CO$_2$-C equilibrium, which can be represented by the Boudouard reaction (Eq. (1)) [15]. This figure is drawn using thermodynamic data from a thermodynamic software package [16]. It illustrates that depending on the reduction temperature, the reduction of Fe$_2$O$_3$ to metallic Fe could adopt a two-step (<550 °C) or three-step mechanism (>550 °C) with the increase of the partial pressure of CO, admitting that in an actual Fe$_2$O$_3$ reduction process, the reduction mechanism could be largely different from the thermodynamic prediction and be more complicated due to the contributing factors mentioned above. It has generally been accepted that the indirect reduction of iron oxides with CO dominates the reduction in a blast furnace as well as in the direct reduction processes producing sponge iron, the solid-solid direct reduction playing only a minor role [17]. And conclusion has been made that for those reduction processes with carbon or carbon monoxide as the reductant, the reversible Boudouard reaction could display a strong controlling influence on the reaction kinetics and mechanism [18-20]. However, there are studies [21-23] in which NiO was reduced by pyrolytic and natural graphite showing that the direct reduction played a major role, and the reaction occurred mostly at the edge surface than at the cleavage surface of the graphite due to the much higher number of active carbon sites on the former where reduction took place preferably. This suggests that the nature of the carbon source (graphite, charcoal, coke, etc.) could also have a significant impact on the kinetics and mechanism of reduction.

\[ C(s) + CO_2(g) = 2CO(g) \]  

(1)

2. Experimental

2.1 Materials

The leach residue for investigation is primarily composed of hematite (Fe$_2$O$_3$ with varying concentrations of Ni as impurities), nickel ferrite (NiFe$_2$O$_4$) and siliceous gangue. Table 1 shows the chemical and mineralogical compositions of the material. Particle size analysis shows 100% below 100 μm with a major portion in the 5–40 μm range. Fig. 2 displays the backscattered electron (BSE) image of the leach residue [3]. It comprises three types of particles: (1) hematite particles with its characteristic porous columnar microstructure (e.g. particle a in Fig. 2); (2) ring-shaped particles containing nickel ferrite and hematite (e.g. particle b in Fig. 2; Ni$_3$S$_2$ resides within some of the ring-shaped particles shown as bright areas); (3) siliceous gangue containing Fe, Mg, Al (e.g. particle c in Fig. 2).

2.2 TG/DTA study
All reduction experiments were conducted in a Setaram TG-DTA 92 unit (SETARAM Inc., Newark, CA). For the reduction with CO, non-isothermal reduction tests at 15 °C/min from room temperature to 1400 °C were performed in both TGA and DTA modes in 1 L/min pure CO gas (CO₂<100 ppm, O₂<100 ppm). Leach residue of typically 50 mg was loaded into an alumina crucible (I.D. 7.2 mm) for TGA runs, whereas the sample size was 15 mg for DTA runs using alumina crucibles (I.D. 4.1 mm). Calcined Al₂O₃ powder of 15 mg was used as reference for DTA runs. The gaseous reduction product CO₂ was continuously swept away by the flow of CO, and the offgas was continuously analyzed for its CO₂ concentration using a gas analyzer (ABB EL3020). Isothermal reduction tests in the temperature range from 400 °C to 1300 °C were also carried out using CO. For each isothermal test, the sample was raised at 15 °C/min to the target temperature in 1 L/min argon, followed by the reduction using 1 L/min CO gas.

Two series of reduction tests were also performed using graphite as the reductant. The graphite powder was produced by grinding a purified (ash content <50 ppm) graphite rod and the fraction below 25 μm was used. The powder and the leach residue were well blended with the weight ratio of 2:5 to provide excess carbon for complete reduction. 70 mg of the mixture (50 mg residue + 20 mg graphite) was used for each TGA run, whereas the sample size for the DTA run was 21 mg (15 mg residue + 6 mg graphite). Non-isothermal reduction of the mixture was conducted in both TGA and DTA modes at 15 °C/min to 1500 °C in 1 L/min argon flow. The offgas was continuously analyzed for its CO and CO₂ content. The isothermal reduction tests were performed for a temperature range of 800–1400 °C in the following manner: The sample mixture was loaded in an alumina crucible, and was first suspended from the micro-balance well above the hot zone of the TGA chamber. The chamber was then heated to the target temperature at the rate of 15 °C/min while being purged with argon (1 L/min), to prevent air ingress. After the target temperature was reached, the sample was quickly lowered into the chamber with continued purge of 1 L/min argon. Because of the small sample size used, the sample was instantly heated to the target temperature by radiation received from the chamber and the reduction was initiated.

2.3 Analytical methods

Reduced products from the experiments were mounted into epoxy, grinded and polished for the observation of their microstructures and for phase identifications using scanning electron microscope (SEM, JEOL JSM-840) which is complemented by an EDS detector. Elemental analysis of the phases in the reduced samples was conducted using an electron probe X-ray microanalyzer (EPMA, Camea SX50). Samples were also analyzed by X-ray powder diffractometer (XRD, Philips PW2273/20) using Cu-Kα radiation for their qualitative mineralogical composition.

3. Results and discussion

3.1 Reduction with CO

3.1.1 Non-isothermal reduction

The leach residue was firstly reduced with CO in both TGA and DTA modes, the results of which are plotted in Fig. 3 as a function of temperature. As can be seen, the reduction is negligible below 400 °C. Most reduction occurred in the temperature range 400–800 °C. In this temperature range, two stages of reduction could be identified. The first stage reduction is denoted by the initial quick mass loss between
400 and 520 ºC, corresponding to two partly overlapped CO₂ peaks at 424 ºC and 455 ºC. There is an endotherm at 405 ºC shown on the DTA curve (heat flow curve). This endotherm should represent the first stage reduction reaction. However, there is a temperature discrepancy for this reduction measured by TGA and DTA. This discrepancy is caused by the geometrical difference of the crucibles used for TGA and DTA as well as the porous nature of the sample which tends to delay heat transfer. This discrepancy was also observed and discussed in previous studies [3, 24]. The second reduction stage occurred between 520 and 800 ºC which is characterized by a quicker mass loss to reach -23.5 wt% with a corresponding large CO₂ peak and an endotherm at 593 ºC.

In order to identify what reduction reactions occurred in these two stages, samples were collected from intermediate temperatures of 520 ºC and 800 ºC and were subject to XRD analysis. Their XRD patterns are plotted in Fig. 4 along with the pattern for the original leach residue for comparison. As can be seen, the phases identified in the original leach residue are hematite and nickel ferrite. Hematite disappeared after the sample was heated to 520 ºC with the formation of substantial amount of magnetite (Fe₃O₄). The formation of an alloy phase Fe₁₀₄Ni is also observed. It becomes evident that one of the reactions in the first stage is the reduction of hematite by CO to magnetite, which could be represented by Eq. (2). By calculation, Eq. (2) could only cause 1.5 wt% mass loss. This suggests that the first small CO₂ peak at 424 ºC is most likely caused by this reduction reaction. The second reaction which is represented by Eq. (3) is responsible for the formation of the alloy Fe₁₀₄Ni and the appearance of the second CO₂ peak at 455 ºC. Due to the presence of Ni as impurities of varying concentrations in the original hematite phase, reduction via Eq. (2) would result in the formation of an iron-nickel oxide (NiₓFe₃₋ₓO₄) instead of magnetite (Fe₃O₄). As a consequence, the reduction product of Eq. (3) is an Fe-rich alloy phase (Fe₁₀₄Ni) instead of pure Fe. Iron oxide reduction is not complete at 520 ºC as suggested by the presence of substantial amounts of magnetite at this temperature, Fig. 4. Relatively broad peaks for magnetite phase, which partly overlap with those for NiFe₂O₄, can be seen at 520 ºC in Fig. 4. This is due to the presence of various amounts of Ni in this phase (NiₓFe₃₋ₓO₄) which caused the distortion of the lattice structure to varying degrees, thereby shifting and/or broadening the XRD peaks. The completion of iron oxides reduction is marked by the disappearance of the magnetite peak at 800ºC, indicating that magnetite reduction proceeds in both reduction stages (400–520 ºC, 520–800 ºC). This is probably caused by the presence of two morphologies of the original hematite phase which gives rise to the difference in their reduction kinetics. The first type has a rather porous columnar structure (e.g. Particle a in Fig. 2), which has easy access to the reduction gas. The second type is relatively dense and co-exists with nickel ferrite in the ring-shaped particles (e.g. Particle b in Fig. 2). The reduction of the latter particles should be slower because of the dense nature of solid phase(s). As a result, it is tentatively suggested that the reduction of the porous magnetite occurred at around 455 ºC, and the denser magnetite in the ring-shaped particles was reduced in between 520 and 800 ºC.

\[
\begin{align*}
3\text{Fe}_2\text{O}_3(s) + \text{CO}(g) &= 2\text{Fe}_3\text{O}_4(s) + \text{CO}_2(g) \quad &\text{(2)} \\
\text{Fe}_3\text{O}_4(s) + 4\text{CO}(g) &= 3\text{Fe}(s) + 4\text{CO}_2(g) \quad &\text{(3)}
\end{align*}
\]

In the second reduction stage (520–800 ºC), nickel ferrite is also reduced, as indicated by the disappearance of nickel ferrite and the formation of an alloy phase Fe₀.₆₄Ni₀.₃₆ in Fig. 4. The reduction of nickel ferrite could be represented by Eq. (4).

\[
\text{NiFe}_2\text{O}_{4}(s) + 4\text{CO}(g) = \text{Fe}_2\text{Ni(allyl)} + 4\text{CO}_2(g) \quad &\text{(4)}
\]
Further increase in temperature above 800 °C caused little mass loss before 1200 °C. On the contrary, a slight mass gain is observed in this temperature range, which is believed to be caused by the carbon deposition onto the sample and the crucible by the reverse Boudouard reaction (Eq. (1)). The gradual drift of the base of the CO$_2$ curve in Fig. 3 also indicates the occurrence of the reverse Boudouard reaction. The base of the heat flow curve in Fig. 3 has drifted, which is caused by the physical changes of the sample during the course of reduction, i.e. decrease in the heat capacity of the sample and/or increase in its thermal conduction rate partly due to the shrink of the sample bed.

Further mass loss occurred after 1200 °C, following an endothermic peak. A previous study [3] showed that the silicate materials in the sample melted at around 1200 °C, suggesting that the reduction of the Fe from the molten silicates (Eq. (5)) should be responsible for this mass loss. The reduced product Fe should be in the form of alloy by merging with the existed alloy phases.

$$\text{Fe}_2\text{SiO}_3(\text{l}) + 2\text{CO}(\text{g}) = 2\text{Fe}($$\text{alloy}) + \text{SiO}_2(\text{s}) + 2\text{CO}_2(\text{g})$$  \hspace{1cm} (5)

### 3.1.2 Isothermal reduction

Isothermal tests were performed to evaluate the reduction kinetics at various temperatures in the range 400–1300 °C. The mass changes were plotted in Fig. 5. As can be seen, the reduction rate increased with the increase of temperature from 400 to 1100 °C indicated by the greater slope of the mass change curve at higher temperatures. At 1100 °C, the reduction was complete within around 3 min. The occurrence of the reverse Boudouard reaction (Eq. (1)) is seen in the isothermal reduction runs in the temperature range 800–1100 °C which is revealed by the slight mass gain after the reduction is complete or near complete. Two distinct reduction stages could be clearly identified for the isothermal run at 1200 °C. At this temperature, the reduction rate is high and comparable to those at 1000 and 1100 °C in the first 45 seconds. A sudden drop in the reduction rate took place at 45 seconds, after which the reduction is slow and only comparable to that at 400 °C. As discussed earlier that the silicates material in the sample begins to melt at around 1200 °C. This sudden drop in the reduction rate is believed to be caused by the melting of the silicates in the sample. In the first stage where the reduction is fast, the sample is rather porous due to the presence of large volume percentage of oxides as solid particles even though the silicates may have melted. Substantial melting of silicates at around 45 seconds results in the collapse of the porous structure, as well as pore blockage by liquid, both of which lead to significant reduction in the reactive surface area. The diffusion through the molten silicates can soon become the rate controlling step, hence the sudden drop in the reduction rate. This phenomena was also observed when using hydrogen as the reductant in the previous study [3]. This sequence of events resembles the reduction of iron ore in the blast furnace when fayalitic liquid is formed as a coating layer on the ore surface, severely limiting the reduction rate in a phenomenon known as slag blocking [25]. At 1300 °C, the quick reduction stage is even shorter. But due to the higher diffusion rate in the silicate melt, the reduction is faster compared with the reduction at 1200 °C in the second reduction stage.

The kinetics of the isothermal reduction was evaluated by analyzing the mass change curves in Fig. 5. Eq. (6) [26] was adopted for this purpose, in which $\alpha$ is the extent of reduction and $t$ is time. The left side of the equation represents the rate of reduction, which is affected by two variables, i.e. temperature ($T$) and extent of reduction ($\alpha$). Arrhenius equation (Eq. (7)) was used to describe the temperature dependence. The dependence of reduction rate on the extent of reduction is represented by the kinetic model $f(\alpha)$, the form of which is determined by its rate controlling mechanism. For an isothermal program, the integral
form of the kinetic model \(g(\alpha)\) has the relationship with temperature \((T)\) and time \((t)\) which is expressed as Eq. (8) [26]. Isoconversional (model-free) method was firstly employed to calculate the apparent activation energies without determining the kinetic models. Eq. (9) can be easily derived from Eq. (8), in which \(t_{\alpha,i}\) represents the time required to reach certain extent of reduction \((\alpha)\) at temperature \((T_i)\). Apparent activation energy at certain extent of reduction can be calculated from the slope of the plot \(\ln t_{\alpha,i}\) v.s. \(1/T_i\). The mass change curves for the isothermal reduction tests at 700–1100 ºC were evaluated by applying Eq. (9) at various extents of reduction \((\alpha)\, 0.2–0.9\). Evaluation was not performed for \(\alpha\leq0.2\) because of the relatively large error arising from the ambiguity in determining the starting time of the reduction from the TGA curves. Apparent activation energies were calculated and plotted against \(\alpha\) in Fig. 6. The plot of \(\ln t_{\alpha,i}\) v.s. \(1/T_i\) is also shown in Fig. 6 as an inset. As can be seen, the apparent activation energy increases from 6.7 kJ/mol to 41.1 kJ/mol with the progress of the reduction. This large variation of apparent activation energy suggests that these \(E_a\) are composite values resulting from the tangled interplay of different steps/processes. These steps/processes could be species-dependent chemical steps, gaseous reactants/products diffusion through a solid product/reactant, adsorption–desorption of gaseous products/reactants on the surface of the reacting solid, etc. [27, 28]. The apparent activation energies are relatively low, indicating the rate controlling mechanism is very likely diffusion control rather than chemical control. In order to determine whether the diffusion of CO through the pores of the sample bed is the rate-controlling factor, two series of TGA experiments were performed. In the first series of experiments, 50 mg leach residue was isothermally reduced at 800 ºC with varying flowrates of CO. The results are plotted in Fig. 7. As can be seen, three mass change curves overlap, indicating that the transfer of CO to the surface of sample bed at 1 L/min was high enough and did not adversely affect the reduction rate. Variation of sample size was then evaluated in the second series of isothermal experiments at 800 ºC, the results of which are shown in Fig. 8. Higher reduction rate can be observed with smaller sample size especially within the first minute of reduction, indicated by the varying slopes of the mass change curves. This suggests that the reduction did not take place uniformly in the sample bed, which resulted from the limited mass transfer (gaseous transfer) in the pores of the sample bed during reduction. The effect of this rate controlling mechanism gradually diminished with the progress of reduction, as suggested by the parallel of the curves after approximately 1 minute.

\[
\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \tag{6}
\]

\[
k(T) = A \cdot \exp\left(-\frac{E_a}{RT}\right) \tag{7}
\]

\[
g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \cdot \int_0^\alpha \exp\left(-\frac{E_a}{RT}\right) dt = A \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot t \tag{8}
\]

\[
\ln t_{\alpha,i} = \ln \left[\frac{g(\alpha)}{A_{\alpha}}\right] + \frac{E_a}{RT_i} \tag{9}
\]

Model fitting method was also used to further determine the rate controlling mechanism. Linear trends are obtained between the reduction rate and \(f(\alpha)\) for the isothermal tests in the temperature range 500–1100 ºC by employing the 2D diffusion model, which is represented by Eq. (10) [26]. These linear trends are
exhibited in Fig. 9 as an inset. For each individual test, 2D diffusion model applies only when \( \alpha \) is higher than a certain value, which is shown in Fig. 9. This is because in the lower range of \( \alpha \), reduction rate is predominantly controlled by the gaseous diffusion in the pores which is discussed earlier. Since the 2D diffusion model represents the diffusion in the solid product layer [29], this indicates that in the higher range of \( \alpha \) where 2D diffusion model applies, diffusion of reactive species through metallic alloys in individual particles controls the reduction rate. Arrhenius plot is also shown in Fig. 9 yielding the apparent activation energy of 31.8 kJ/mol based on the slope of the line. This corresponds to a value when \( \alpha \) is approximately 0.8 in Fig. 6. The plot for 500 ºC deviated from the linear trend in Fig. 9. This deviation is possibly caused by the partial reduction at low temperatures due to the stepwise reduction mechanism (Eqs. (2–4)), whereas at other higher temperatures the reduction is near completion. From the above discussion, gaseous diffusion through the pores of the sample bed mainly controls the reduction rate at lower range of \( \alpha \), and the rate controlling factor gradually shifts to the diffusion through the layer of alloy products in individual particles at higher range of \( \alpha \). Large variation of activation energies with \( \alpha \) in Fig. 6 is a result of the combining effect of the two rate-controlling mechanisms as well as their varying contributions to the overall reduction rate.

\[
f(\alpha) = -\ln(1-\alpha)^{1} \quad (10)
\]

The reduction products from the isothermal tests were examined by SEM/EDS. Fig. 10 illustrates the microstructures of the porous hematite particles after reduction by CO at various temperatures. The hematite was not reduced at 400 ºC and its columnar porous structure was preserved (top-left). At 500 ºC, the hematite was reduced to form highly porous Fe particles with submicron grains (top-right). The grains grow coarser and further apart when reduced at higher temperatures (bottom-left and bottom-right). Some sintering could be observed in the reduced hematite particles at 900 ºC.

The change of morphologies of the ring-shaped particles reduced at various temperatures was also examined and is presented in Fig. 11. Nickel sulfide resided within some of the ring-shaped particles, which can be seen in Fig. 11. The particle at 400 ºC in Fig. 11 was not reduced. And the oxide ring is much denser compared with the hematite particle in Fig. 10. Reduction was obvious when the temperature reached 500 ºC and the ring formed Fe-Ni alloy with micron-sized pores. At 600 and 700 ºC, the alloy rings were still rather porous, and the residual nickel sulfide was partly converted to nickel-rich Ni-Fe alloy. This reaction is tentatively suggested as the reduction of the nickel sulfide to form alloy with carbonyl sulfide (COS) as the gaseous product, which is represented by Eq. (11). Crowe and Utigard [30] have reported this reaction as being responsible for the reduction of Ni, Cu, and Co sulfides by CO. Above 800 ºC in Fig. 11, substantial sintering took place, and the degree of sintering is greater at higher temperatures. For the sample reduced at 900 ºC, some Fe$_2$O$_3$ was found locked in the alloy phase. This was caused by the immediate sintering of the alloys that were formed on the surface of the oxide which limited the reduction rate of the oxide. The residual nickel sulfide was fully reduced to nickel-rich alloy which sintered on the alloy ring. At 1100 ºC, the reduced ring was adequately densified and formed a uniform alloy particle.

\[
\text{Ni}_3\text{S}_2(s) + 2\text{CO}(g) = 3\text{Ni(alloy)} + 2\text{COS}(g) \quad (11)
\]

The silicates melted at 1200 ºC and all pores were removed. The alloy phase formed during this process was distributed in the silicate melt as small particles of various shapes. Two silicates were formed from the exsolution of the melt upon cooling, i.e. pyroxene which is rich in Fe and Al, and olivine which is rich
in Fe and Mg. The silicates phases formed were found to have higher Fe content than the original silicates in the leach residue before reduction. This suggests that part of the iron oxide in the leach residue must have dissolved into the silicate melt. This is further supported by the fact that a large number of small regular-shaped Fe$_2$O$_3$ particles were exsolved from the silicate melt upon cooling, which could be seen in the BSE image at 1200 °C in Fig. 11. The partial dissolution of the hematite into the silicate melt which substantially lowered the activity of hematite might be another critical factor that led to the slow reduction rate at 1200 °C (Fig. 5). In this case, the reduction is better represented by Eq. (5) in which Fe is formed from the reduction of the silicate melt and merges with the existing alloy particles. At 1300 °C, more alloys were formed and the two silicate phases (pyroxene and olivine) exsolved from the melt formed a laminar structure with no exsolution of Fe$_2$O$_3$ particles. This is probably caused by the greater degree of reduction at higher temperature which resulted in an iron-deficient silicate melt. During reduction, gas bubbles of CO$_2$ were formed, which on solidification left behind features such as those seen in Fig. 12. Upon cooling the melt, the gas bubbles shrink in volume, drawing the still-liquid silicate phase from the already sintered alloy particles. On complete solidification, a spherical void and an alloy-free halo remain at the bubble site. Because the exsolved pyroxene phase has a higher freezing temperature than the olivine phase, the pyroxene solidifies before olivine, creating the unique laminar structure with parallel plates of olivine separated by a gap, Fig. 12.

3.2 Reduction with graphite

3.2.1 Non-isothermal reduction

Fig. 13 shows the results for the reduction of the leach residue with excess amount of graphite powder by continuously heating the mixture of the two at 15 °C/min to 1500 °C under argon atmosphere. As can be seen, little reduction occurred below 800 °C. Higher temperature (>800 °C) is required to initiate the reduction using graphite as reductant compared with the reduction using CO (>400 °C). This is possibly due to the different reduction mechanisms involved: initial reduction of the oxides by graphite is solid-solid reaction which has very limited reaction sites, with much smaller rate than the gas-solid reaction involving CO. Moreover, even with the same area of reaction sites for two cases, the different reduction mechanisms determine that the effect of temperature on the progress of reduction for both cases must be different. Above 800 °C in Fig. 13, the reduction progressed gradually, resulting in an increasing mass loss and the formation of mainly CO$_2$ as the gaseous product below 1000 °C. Massive reduction took place above 1000 °C peaking at 1050 °C, which resulted in large emission of CO and CO$_2$. DTA analysis measured a large endotherm at 1020 °C which corresponds to this stage of reduction. The main reduction reactions occurred in this stage are the reduction of hematite and nickel ferrite, represented by Eqs. (12–17). Gas-solid reduction reactions which are represented by Eqs. (14) and (17) are expected to take place due to the formation of CO from Eqs. (12) and (15) as well as from the Boudouard reaction (Eq. (1)). The following scenario can be envisaged. The gas (CO and CO$_2$) formed from within the sample bed needs to diffuse upwards to the surface of the bed before it is swept away by the argon flow. As the CO and CO$_2$ formed diffuse upwards through the pores of the sample bed, CO component could reduce oxides on its path (Eqs. (14) and (17)), resulting in an increased partial pressure of CO$_2$. While the CO$_2$ component could be reduced by the graphite particles on its path depending on the equilibrium of the Boudouard reaction (Eq. (1)), resulting in the increased partial pressure of CO. The reversed Boudouard reaction could also take place if the partial pressure of CO is higher than equilibrium. As a result, the relative partial pressure of CO and CO$_2$ in the offgas analyzed (Fig. 13) is a result of the competition among the
reversible Boudouard reaction (Eq. (1)), reduction reactions by graphite (Eqs. (12), (13), (15), (16)), and
reduction reactions by CO (Eqs. (14) and (17)). Due to the complexity of the reaction system, no further
effort was made to determine which type of reaction prevailed in the reduction process.

The Boudouard reaction, Eq. (1), was also expected to take place. The speculation is made based on the
fact that in Fig. 13, the formation of CO2 as the gaseous reduction product predominates below around
1000 °C, above which the formation of CO prevails. This trend is in accordance with the equilibrium of
Boudouard reaction (Fig. 1), although the offgas CO/CO2 in Fig. 13 did not reach equilibrium because of
the non-equilibrium conditions applied. The reduction slowed down until the temperature reached 1200
°C, above which a second stage quick reduction occurred. It peaked at 1300 °C and ended at 1340 °C. This
second stage of reduction resulted in the formation of CO as the gaseous product and corresponds to an
endotherm peak at 1235 °C. This is believed to be induced by the melting of the silicates in the sample
which caused the reduction of the molten silicate by the graphite, which could be represented by Eq. (18).

\[
\begin{align*}
\text{Fe}_2\text{O}_3(s) + 3\text{C}(s) &= 2\text{Fe}(s) + 3\text{CO}(g) \\
2\text{Fe}_2\text{O}_3(s) + 3\text{C}(s) &= 4\text{Fe}(s) + 3\text{CO}_2(g) \\
\text{Fe}_2\text{O}_3(s) + 3\text{CO}(g) &= 2\text{Fe}(s) + 3\text{CO}_2(g) \\
\text{NiFe}_2\text{O}_4(s) + 4\text{C}(s) &= \text{NiFe}_2(\text{alloy}) + 4\text{CO}(g) \\
\text{NiFe}_2\text{O}_4(s) + 2\text{C}(s) &= \text{NiFe}_2(\text{alloy}) + 2\text{CO}_2(g) \\
\text{NiFe}_2\text{O}_4(s) + 4\text{CO}(g) &= \text{NiFe}_2(\text{alloy}) + 4\text{CO}_2(g) \\
\text{Fe}_2\text{SiO}_4(l) + 2\text{C}(s) &= 2\text{Fe}(s,l) + \text{SiO}_2(s) + 2\text{CO}(g)
\end{align*}
\]

3.2.2 Isothermal reduction

In order to study the reduction kinetics at different temperatures, isothermal reduction tests were
performed in the temperature range 800–1400 °C with the results shown in Fig. 14. And the reduction
products from these isothermal runs were examined by SEM/EDS, EPMA, and XRD to elucidate the
reduction mechanisms. As can be seen in Fig. 14, at low temperatures of 800 and 900 °C, the reduction
rate is slow and very limited reduction took place within 30 min. Effective reduction only occurred when
the temperature is higher than 1000 °C. Two quick reduction stages can be observed at this temperature,
which took place during 0–2 min and 4–7 min, respectively. This possibly resulted from the sequential
reduction of the porous hematite particles and the relatively dense ring-shaped particles which are
composed of both hematite and nickel ferrite. The reduction at 1100 °C was faster and near complete
within 3 min. Two stages of reduction were also observed for the isothermal runs at and above 1200 °C.
In this case, the first stage is always the quick reduction of the oxides until approximately 25 wt% mass
loss is reached, while the following second stage is the reduction of the molten silicate. It is apparent from
Fig. 14 that the molten silicate reduction stage is faster at higher temperatures, indicated by the higher
slope of the curves below -25 wt% at higher temperatures.

The alloy phases that were formed from these isothermal runs were analyzed by EPMA and the results are
presented in the ternary graph in Fig. 15. The alloy phases identified at 900 °C under the electron probe
are all nickel-rich Ni-Fe alloys, which are formed from the reduction of the nickel sulfide. Previous study
showed that the nickel sulfide (Ni$_3$S$_2$) melted at 813 ºC [24]. As a result, it was in its molten state during isothermal reduction at 900 ºC. The reaction is tentatively represented by Eq. (19). Reduction by CO (Eq. (11)) could also take place if appreciable CO is present in the sample bed. Fig. 16 (a) exhibits a partly reduced nickel sulfide particle forming nickel-rich alloy with a clear boundary between the alloy and sulfide phases. Another alloy particle is shown in Fig. 16 (b) as the product from the reduction of the nickel sulfide at 1000 ºC. It is evident from this particular morphology that both the alloy and the nickel sulfide were in liquid state during reduction, the sulfide covering the surface of the alloy drop.

\[
\text{Ni}_3\text{S}_2(l) + \text{C}(s) = 3\text{Ni(alloy)} + \text{CS}_2(g)
\]  

(19)

With the further increase of temperature, more iron-rich alloys were formed from the reduction of the hematite and nickel ferrite, which can be seen from Fig. 15. Reduction of the silicates started at 1200 ºC denoted by the presence of around 15 at% Si in the alloy phase. The silicates after isothermal reduction were also analyzed by EPMA to reveal the progress of reduction, which is plotted in Fig. 17. The near depletion of the iron from the silicates at 1200 ºC indicates that Fe is also reduced along with Si. The reduction of Fe from the silicate is more complete at 1200 ºC and higher. The SiO$_2$ content of the silicates also dropped with the increase of temperature, indicating a larger extent of reduction at higher temperatures in terms of Si removal. Fig. 18 (a) exhibits the nucleation and growth of Fe–Si alloy particles within the silicate melt. The sizes of the particles range from nanometers to microns. The exterior Fe-Ni alloy gradually absorbs some of these Fe-Si particles, particularly from the edge of the silicate, to form a Fe-Ni-Si phase. Fig. 18 (b) shows a Fe-depleted silicate particle covered with a relative thick layer of Fe-Ni-Si alloy at 1200 ºC. This suggests that the reduction of silicate melt could also proceed by the diffusion of carbon or possibly CO through the alloy.

With the increase of the isothermal temperature from 1200 to 1400 ºC, the composition of the alloy particles becomes more uniform, suggested by the converging trend of the plots in Fig. 15. This indicates that alloy particles have a greater tendency to merge and form larger and more uniform particles at higher temperatures, which is supported by the evidence from both the SEM and XRD analysis. Fig. 18 (c) shows the spherical alloy particles produced at 1300 ºC. These particles could be as big as 100 µm in diameter. Fig. 18 (d) shows an alloy particle 175 µm in diameter. Two phases were exsolved from the alloy melt showing different grey levels. The interior brighter phase has more Fe and less Si. XRD analysis was conducted on the samples produced from the isothermal runs at 1000 ºC, 1200 ºC and 1400 ºC with the results shown in Fig. 19. At 1000 ºC, the main alloys are Fe$_{0.64}$Ni$_{0.36}$ and Fe$_{10.8}$Ni which were produced from the reduction of the nickel ferrite and hematite, respectively. Due to the reduction of molten silicate, Fe-Ni-Si alloy formed as the major alloy phase at 1200 ºC with minor amount of Fe$_{0.64}$Ni$_{0.36}$. The alloy produced at 1400 ºC is a relatively homogeneous phase of Ni-Si-Fe, showing enhanced merging of the alloy particles.

4. Conclusions

Reduction of the leach residue by both carbon monoxide and graphite was conducted using TGA and DTA. The reduced products were analyzed by SEM/EDS, EPMA and XRD. Results show that the reduction by CO initiated at around 400 ºC during the non-isothermal reduction tests. The reduction of the hematite phase took place in two stages with magnetite as the intermediate products. Nickel ferrite was
reduced mostly in between 520 and 800 °C resulting in the formation of an alloy phase Fe$_{0.64}$Ni$_{0.36}$. Significant sintering of the alloys was observed above 800 °C, and the extent of the sintering was greater at higher temperatures. Below 1200 °C, the isothermal reduction was firstly controlled by the gaseous diffusion in the pores of the sample bed. More alloy products formed with the progress of reduction, resulting in the gradual shift of the rate-controlling mechanism to the diffusion through the alloy products in individual particles. This change of rate-controlling mechanism led to the increase of the apparent activation energies from 6.7 kJ/mol ($\alpha=0.2$) to 41.1 kJ/mol ($\alpha=0.9$). The siliceous gangue melted at 1200 °C, which caused the partial dissolution of hematite into the silicate melt and removal of pores from the sample bed. This resulted in slow reduction kinetics.

Substantial reduction of the leach residue by graphite powder took place only above 1000 °C. The formation of CO or CO$_2$ as the main gaseous product is largely dependent on temperature, and is suggested to be dominantly influenced by the Boudouard reaction. The Fe and Si components of the silicates could be reduced by graphite above their melting temperature (1200 °C) forming an Fe-Si alloy. The alloys formed from the reduction of hematite, nickel ferrite or silicates tend to be more homogeneous at higher temperatures resulting from the enhanced merging of the alloy particles.

Acknowledgements

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References


Figures
Fig. 1. Stability diagram for Fe-O system under CO-CO$_2$ atmospheres (solid lines) and CO partial pressure established by the Boudouard reaction (dashed line).

Fig. 2. BSE image of the leach residue [3].
Fig. 3. Non-isothermal reduction (15 °C/min) of the leach residue in CO.

Fig. 4. XRD patterns for the leach residue (a), and samples collected after non-isothermal reduction in CO to 520 °C (b) and 800 °C (c).
Fig. 5. TGA isothermal reduction of the leach residue with CO.

Fig. 6. Variation of apparent activation energies as a function of extent of reduction ($\alpha$) for the isothermal reduction tests. $\ln t$ v.s. $1/T \times 10^4$ (isocconversional method) is also plotted as an inset.
Fig. 7. Effect of the variation of the flowrates of CO on the isothermal reduction of the leach residue.

Fig. 8. Effect of the variation of sample sizes on the isothermal reduction of the leach residue.
Fig. 9. Arrhenius plot for the isothermal reduction tests between 500 and 1100 °C. The relationship between the reduction rate and the 2D diffusion model \( f(\alpha) = -\ln(1-\alpha) \) is also plotted as an inset.

Fig. 10. Isothermal reduction of the porous hematite particles with CO at various temperatures.
Fig. 11. Microstructure of particles reduced by CO under isothermal conditions (Px: Pyroxene, silicate containing Fe, Al, Na; Ol: Olivine, silicate containing Fe, Mg).

Fig. 12. Laminar structure of the silicates formed upon cooling the reduced residue from 1300 °C with a gas bubble formed in the melt (left) and interior of the bubble (right).

Fig. 13. Non-isothermal reduction (15 °C/min) of the leach residue with graphite in TGA and DTA.

Fig. 14. TGA isothermal reduction of the leach residue with graphite.
Fig. 15. EPMA analysis on the alloy particles formed from the isothermal reduction tests by graphite.

Fig. 16. (a) Partial conversion of the nickel sulfide to alloy at 900 ºC; (b) Alloy surrounded by monosulfide solid solution (Mss, (Ni,Fe)S) reduced at 1000 ºC (Px: Pyroxene, silicate containing Fe, Al).

Fig. 17. The composition of silicate phases in isothermal reduction by graphite.
Fig. 18. (a) Formation of Si$_x$Fe alloy particles from the silicate melt at 1200 °C (Px: Pyroxene, silicate containing Al, Mg, Fe); (b) Reduction of Fe and Si from a silicate particle forming Ni-Si-Fe alloy at 1200 °C (Px: Pyroxene, silicate containing Al, Mg, Na); (c) Ni$_x$Si$_y$Fe alloy formed at 1300 °C; (d) An Ni$_x$Si$_y$Fe alloy particle formed from the reduction at 1400 °C.

Fig. 19. XRD analysis on the product from the reduction at 1000 °C, 1200 °C and 1400 °C.

Table
Table 1. Chemical and mineralogical compositions of the leach residue.

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<th>Fe</th>
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<th>S</th>
<th>Cu</th>
<th>Co</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
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