Carbon Dissolution Occurring during Graphite–Ferrosilicon Interactions at 1 550°C

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The carburisation reaction is a key reaction for the cupola process, since the metallic liquid droplets interact with coke at high temperatures. The kinetic mechanism of carbon dissolution in liquid iron had been extensively investigated. However, there is little knowledge about the kinetics of carbon dissolution when the silicon contents are over 10 %, since the silicon content during the iron and steel making processes are usually well below this limit.

Carbon dissolution phenomenon and associated mechanisms are established for ferrosilicon alloys and silicon at 1 550°C in this study. The overall-rate constants at 1 550°C for Si 98.5 %, FeSi 74 % and FeSi 24.7 % were 3.8 , 3 and $3.9 \times 10^{-3} \text{ (s}^{-1}\text{)}$ respectively. The appearance of SiC as an interfacial product was found during the metal–graphite interactions and its role as a retarding agent during the carbon pickup was established.

The kinetics of carbon dissolution from graphite is controlled by a mixed-control mechanism and this includes the diffusion of carbon and carbon transfer from the SiC interfacial layer.

KEY WORDS: ferrosilicon; graphite; carburisation; kinetics.

1. Introduction

Despite technological advances in cast iron manufacturing in recent years, the cupola process still offers several competitive advantages. The lower operating cost, higher tolerance for harmful trace elements, and a wider range for iron-production rates makes this technology an attractive alternative for cast iron manufacturers.¹⁾

Alternative layers of coke, iron and steel scrap, fluxes and ferroalloys are added continuously during the cupola process. The upward flow of hot gases transfer heat to the metallic charge, which causes its melting and subsequent interaction with the coke lumps.

Ferrosilicon reactions play a key role during this process. Since the amount of silicon coming from the recycled metal is usually low, the addition of some ferrosilicon alloy is required in order to achieve the desired composition in the final product. Silicon is usually added into the furnace as ferrosilicon lumps with up to 75 wt% Si. The amount of ferrosilicon added to the cupola accounts for around 1.2–2 % of the total metallic charge.²⁾

Coke is also an important component of the metallic charge, playing two important roles. In the cupola process, the major exothermic reaction involves the carbon contained in the coke and the oxygen in the blast. The combustion reactions provide the required amount of heat to melt the scrap metal and keep the liquid bath at the desired temperatures. Carbon from coke dissolves into the liquid metal, raising the carbon content to the required levels.

Since the Fe–Si–C system is extremely important for steel makers, several publications exist which report on exhaustive study in the thermodynamics of the system and which have obtained more accurate data and improved the existing phase diagrams.^{3–6)} Other studies^{7–11)} had conducted extensive work on the solubility of carbon in silicon-rich alloys.

The factors governing the carbon dissolution from graphite into molten iron have been well-studied^{12–18)} using both experimental and theoretical approaches and one of the goals of these studies has been to understand the rate-controlling mechanisms. During the cupola process there is significant interaction among the coke lumps and the ferrosilicon alloys forming part of the metallic charge. New findings about the interfacial phenomena in this system have been published¹⁹⁾ but no data has been reported yet on the reaction kinetics during the carbon dissolution in ferrosilicon alloys.

This paper reports on the carbon dissolution phenomena for ferrosilicon alloys and silicon at 1 550°C. The apparent carbon dissolution rates from synthetic graphite into silicon (98.5 %) and ferrosilicon alloys containing approximately 74 and 24.7 wt% Si at 1 550°C were calculated. These results and the findings of associated mechanisms will assist with the development of fundamental understanding of carbon dissolution.

2. Previous Studies

Several authors have addressed the solubility of carbon in silicon, and it has generally been found to be very low.⁷⁻¹¹⁾ Scace *et al.*⁷⁾ reported the solubility of C in liquid Si at temperatures up to 2900°C and proposed a phase diagram for the Si-C system. Nozaki *et al.*⁸⁾ conducted experiments using a silicon semiconductor at the silicon melting point and found a carbon concentration just prior to the appearance of silicon carbide at $3.5 \pm 0.4 \times 10^{17}$ at/cm³. Yanaba *et al.*⁹⁾ found a temperature dependence of the carbon solubility in liquid silicon with the calculated carbon solubility at the melting point of silicon to be at 79 ppm (9.1×10^{18} at/cm³). Ottem¹⁰⁾ obtained thermodynamic data for the solubility of carbon in pure silicon, FeSi75 and FeSi65 at equilibrium with SiC. At 1550°C, the solubility of carbon in Si was found in the range of 150–170 ppm, while values for FeSi75 and FeSi65 (100–120 ppm) and (70–75 ppm) respectively were lower and showed a direct correlation between silicon content and carbon dissolved in the metal. However, at 1614°C, the solubility of C on FeSi increased when %Si was below 50%, reaching solubility values similar to ferroalloys with 90 wt% Si.¹¹⁾ Klevan¹⁰⁾ found a carbon content range of 700–1100 ppm when FeSi75 was tapped from the furnace. Statistical analyses of 779 shipments over 3 years found that the carbon content dropped to an average of 300 ppm C, after crushing and screening the material implying that the carbon, which precipitates as SiC particles as the temperature drops during tapping and handling, is physically removed as particles to a fairly large extent.

The factors governing the carbon dissolution from graphite into molten iron have been well studied. It had been established that carbon dissolution from graphite is a two-step process¹⁸⁾:

1. Dissociation of carbon atoms from their crystal site in the graphite into the carbon/melt interface.
2. Mass transfer of carbon atoms through the adjacent boundary layer into the bulk liquid iron.

Despite the important role of the carbon pickup in the scrap-melting process, the reaction kinetics of the carbon dissolution in silicon-rich alloys are not yet well understood and no data had been reported in the literature for silicon contents greater than 10 wt%.

This paper presents findings of carbon pickup from graphite in silicon 98.5% and ferrosilicon alloys containing 74 and 24.7% Si at 1550°C. An apparent rate constant for each case is calculated and the carbon dissolution mechanism is established. The relationship between carbon dissolution and the interfacial phenomenon is also discussed.

3. Experimental Methods and Materials

The equipment used to conduct the experiments was a horizontal high temperature furnace. It included a 1 m-long and 50 mm inner-diameter high alumina reaction tube with two resistance-heating elements. Three separate temperature indicators, each one with a type B thermocouple were used. One of these thermocouples was placed inside of the

Fig. 1. Schematic of the experimental arrangement.

Table 1. Chemical compositions of materials.

	Fe	Si	C	Al
FeSi24.7	72.6-75.2	24.6-26	0.012-0.034	0.06
FeSi74	22.7-26.7	72.2-76.8	0.015-0.024	0.06

reaction chamber, near the sample, while the other two monitored the furnace temperature (Fig. 1).

The ferrosilicon alloys used in the experiments contained 74 and 24.7 wt% Si respectively. Silicon 98.5% was also used. The chemical composition for the ferroalloys is shown in Table 1.

Synthetic graphite crucibles (2H) ($\phi=10$ mm, $H \approx 12-15$ mm), as well as SiC plates ($45 \times 45 \times 10$ mm) with 85%SiC–15%Si content, were used for the carbon dissolution experiments.

The sample assembly consisted of a stainless steel/alumina rod with an alumina boat attached at the end. Graphite crucibles containing the metallic samples (weighing $\sim 0.4-0.6$ g) were placed into the reaction tube and these were left for varying times (from 30 s up to 6 h) at 1550°C. A high purity argon stream at a rate of 1 L/min was introduced through an inlet at one cap and off-gas was released at the other cap. Sliding the assembly into the cold zone, concluding any further reaction quenched the samples. The number of samples for each experimental data range was between 4 and 6 samples.

The accuracy of the results was dependant on the removal of impurities (graphite particles) from the metal samples. Low-silicon samples were easily removed from the synthetic graphite crucibles, since no strong bond with the substrate was found. The adherence for the high-silicon samples was notably greater hence the separation from the substrate was carried out with extreme care.

Graphite leftovers were cleaned using sand paper (180 μ m), which was placed on a rotating disk. The metal samples used for carbon dissolution on SiC substrates were taken at the metal/substrate boundary using a very fine diamond saw at low speed. The cleaning procedure for these samples was similar as for the graphite removal from the synthetic graphite crucibles. Once the samples were cleaned, carbon analyses were undertaken on the Carbon-Sulphur analyser (LECO* CS 244). The results were processed and plotted, producing graphs for carbon pickup as a function of time for each ferrosilicon alloy and silicon

* LECO is a trademark of the LECO Corporations, St. Joseph, MI.

Fig. 2. Carbon pickup from graphite into pure iron at 1550°C.

samples.

X-ray diffraction (XRD) was also used for interfacial analysis. The metal/graphite interphase was scanned from 25° to 75°, at 1°/min using step size 0.02°/min. The procedure has been described in a previous study.¹⁹⁾

4. Results and Discussion

4.1. Carbon Dissolution from Synthetic Graphite Substrates

An investigation of the kinetics of carbon dissolution from graphite and coke in molten iron has been carried out in the past using the sessile-droplet method.¹⁷⁾ In the current study, samples weighing approximately 0.1 g were placed inside synthetic graphite crucibles. Experimental runs using pure iron were undertaken with the current experimental set up and these showed that the carbon saturation limit in pure iron was 5.57 wt% C. The overall-constant rate obtained from the experimental runs was $4.16 \times 10^{-2} \text{ s}^{-1}$, with both results showing close agreement with previously reported results¹⁷⁾ (Fig. 2).

The plot of carbon pickup for Si 98.5%, FeSi 74% and FeSi 24.7% as function of time are shown on Figs. 3, 4 and 5. Additional windows, showing a detailed view of the initial 3-min period are also included on Figs. 3a, 4a and 5a. It was observed that the carbon content increases within the initial 10 min but these levels remain constant after this increase. The carbon pickup trend showed no significant differences between Si 98.5% and FeSi 74%. A different behaviour was found for FeSi 24.7%, where a sharp increase in carbon content was observed within the first 60 s.

From previous studies¹⁰⁾ it is known that there is a direct relationship between silicon and carbon content in the ferroalloy, showing a trend for silicon content greater than 50 wt%. However, below this limit, carbon dissolved in the metal holds an inverse dependence with the silicon content in the ferroalloy (Fig. 6).

The rapid carbon pickup during the first 3 min suggested a similar kinetic mechanism observed for carbon dissolution in iron. In view of the similarities, a first order kinetic equation was applied for the analysis of the rate constant.

Fig. 3. Carbon pickup from graphite into Si 98.5% at 1550°C.

Fig. 3a. Carbon pickup from graphite into Si 98.5% at 1550°C during the first 3 min.

Fig. 4. Carbon pickup from graphite into FeSi 74% at 1550°C.

Fig. 4a. Carbon pickup from graphite into FeSi 74% at 1550°C during the first 3 min.

Fig. 5. Carbon pickup from graphite into FeSi 24.7% at 1 550°C.

Fig. 5a. Carbon pickup from graphite into FeSi 24.7% at 1 550°C during the first 3 min.

Fig. 6. Solubility of carbon on liquid silicon at different temperatures.¹⁰⁾

$$\frac{dC}{dt} = k(C_s - C_t) \dots\dots\dots(1)$$

After integrating Eq. (1)

$$\int \frac{dC}{(C_s - C_t)} = \int k dt \dots\dots\dots(2)$$

The integrated form of Eq. (2) gives us,

$$\ln \frac{(C_s - C_t)}{(C_s - C_o)} = -kt \dots\dots\dots(3)$$

Where, C_s is the melt carbon saturation; C_t is the instantaneous melt carbon content; and C_o is the initial carbon content.

From plotting $\ln\{(C_s - C_t)/(C_s - C_o)\}$ vs. time t (s), the constant rate k can be deduced graphically. **Figures 7, 8 and 9** show these plots for Si 98.5%, FeSi 74% and FeSi 24.7% runs at 1 550°C on graphite substrates.

FeSi 24.7% achieved the higher carbon saturation (C_s) limit (0.149% C) compared with FeSi 74% (0.105% C) and Si 98.5% (0.116% C). Reported data from the literature¹⁰⁾ also showed lower C_s for FeSi 75% compared to pure silicon.

Rate constants obtained for FeSi 24.7%, FeSi 74% and

Fig. 7. Plot of $\ln\{(C_s - C_t)/(C_s - C_o)\}$ vs. time (s) for carbon dissolution runs of Si 98.5% at 1 550°C.

Fig. 8. Plot of $\ln\{(C_s - C_t)/(C_s - C_o)\}$ vs. time (s) for carbon dissolution runs of FeSi 74% at 1 550°C.

Si 98.5% were 3.9×10^{-3} , 3×10^{-3} and 3.8×10^{-3} respectively, showing direct correlation with C_s values. This also indicates that the diffusion mechanism plays a key role in the initial stages (3 min) of the interfacial reaction.

From previous studies,¹⁹⁾ it was found that an interfacial reaction producing SiC as interfacial product occurs, and that this reaction played a significant role in dynamic wetting. XRD scanning (**Figs. 10–12**) at the interface ferroalloy/synthetic graphite showed the appearance of SiC as in-

Fig. 9. Plot of $\ln\{(C_s - C_t)/(C_s - C_o)\}$ vs. time (s) for carbon dissolution runs of FeSi 24.7% at 1550°C.

Fig. 10. XRD spectra. Interface of Si 98.5%/synthetic graphite after 0, 30 and 1800 s at 1550°C.

Fig. 11. XRD spectra. Interface of FeSi 74%/synthetic graphite after 1, 60 and 1800 s at 1550°C.

terfacial product. Strong peaks of SiC appear 30 s after melting for Si 98.5% and the formation of SiC at the interface of FeSi 74%/graphite was observed 60 s after melting, while for FeSi 24.7%, the SiC was first detected after 15 min.

The experimental result of carbon dissolution runs on SiC substrates is discussed in the next section along with an understanding of the influence of the interfacial SiC formation on the carbon dissolution reaction.

Fig. 12. XRD spectra. Interface of FeSi 24.7%/synthetic graphite after 1, 900 and 1800 s at 1550°C.

Fig. 13. Plot of $\ln\{(C_s - C_t)/(C_s - C_o)\}$ vs. time (s) for carbon dissolution runs of Si 98.5% on graphite and SiC substrates at 1550°C.

Fig. 14. Plot of $\ln\{(C_s - C_t)/(C_s - C_o)\}$ vs. time (s) for carbon dissolution runs of FeSi 74% on graphite and SiC substrates at 1550°C.

4.2. Interfacial Role of SiC during Carbon Dissolution

Experimental runs were carried out on 85% SiC plates using the sessile-droplet method. The experiments were performed under similar conditions to the ones described earlier on synthetic graphite crucible. Comparisons between rate constants on both substrates were plotted for each ferroalloy tested (Figs. 13, 14 and 15).

Fig. 15. Plot of $\ln\{(C_s - C_t)/(C_s - C_o)\}$ vs. time (s) for carbon dissolution runs of FeSi 24.7% on graphite and SiC substrates at 1550°C.

Table 2. Overall rates constant for ferroalloys tested on different substrates (s^{-1}).

	Substrate	
	Synthetic graphite	SiC
Si 98.5%	3.8×10^{-3}	1.7×10^{-4}
FeSi 74	3×10^{-3}	4×10^{-4}
FeSi 24.7	3.9×10^{-3}	8×10^{-4}

As expected, the carbon dissolution rate constant from SiC substrates is, approximately, one order magnitude smaller compared with the rate of carbon dissolution, as shown in **Table 2**. Understandably, the formation of SiC as interfacial product creates some resistance to the carbon diffusion from the graphite substrate and therefore, has a retarding effect on the overall process.

It was also observed that, despite of the similar order of magnitude, the rate constants changed significantly for each composition, since the rate constant for FeSi 24.7% is double that of FeSi 74% and is almost three times that of Si 98.5% (Table 2). This suggests that the process is favoured by lower silicon (or higher iron) contents in the ferroalloy.^{16–18)}

The overall rates of carbon dissolution from graphite are quite similar for each sample. The carbon diffusion process occurs remarkably faster at initial stages but after the initial pickup, the appearance of SiC plays a retarding effect and slowed down the overall process. It can be concluded that the carbon dissolution process in silicon and ferrosilicon alloys is governed initially by diffusion and beyond this stage; the process is governed by mixed control (including interfacial resistance by SiC), which slows down the rate of carbon dissolution. The free diffusion of carbon occurs preferentially during the initial stages of the metal–substrate interaction.

The carbon pickup occurs at similar rates across the ferroalloys and it was commonly observed that the carbon content rapidly increases at early stages. Carbon saturation levels (C_s) are consistent with the rate constant of the carbon dissolution reaction and this suggests that carbon diffusion is the primary mechanism in the initial stage. At the

same time, it was observed that SiC appeared as the interfacial product, providing an interfacial resistance and slowing down the carbon dissolution from graphite.

5. Conclusions

The carbon dissolution from synthetic graphite and the effect of SiC as interfacial product in ferrosilicon alloys was studied. This work was investigating the kinetic mechanism of carbon dissolution reaction.

The following conclusions drawn from the results are:

(1) The overall rate constants do not present significant differences across the samples, suggesting that carbon diffusion is a predominant mechanism controlling carbon dissolution. However, the faster rate in the case of FeSi 24.7% can be explained on the basis of delayed formation of SiC interfacial product.

(2) The appearance of SiC as interfacial product plays a retarding effect on the overall process and dictates the carbon transfer. This layer appears at very early stages of the process for Si 98.5% and FeSi 74%, while it takes longer to be formed for FeSi 24.7%.

(3) The kinetics of carbon dissolution for FeSi 24.7%, FeSi 74% and Si 98.5% is driven by a mixed control mechanism, where both carbon diffusion and interfacial resistance due to SiC formation influence the process.

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