Reaction Mechanism of Ferrosilicon Synthesis Using Waste Plastic as a Reductant

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Reaction mechanism study of ferrosilicon synthesis was carried out by using reagent grade material, graphite and waste plastic, Bakelite as reducing agent over a temperature range of 1 623 K to 1 823 K (1 350°C to 1 550°C) under inert atmosphere. Reaction rate was determined by using off-gases evolving from reduction reactions. Results showed that reduction mechanism was predominantly controlled by chemical reactions with both the reducing agent. Initially Bakelite bearing pellet showed faster reaction rate compared to graphite due to volatiles generation and less crystalline nature of Bakelite derived carbon. Extent of reduction can be improved by increasing temperature; however Bakelite bearing pellet showed lower dependency on temperature compared to graphite. Activation energy for graphite and Bakelite pellet is 238.07 kJ/mol and 140.29 kJ/mol respectively. This comparative study will create new opportunities to use waste Bakelite as a reductant even at moderately lower temperature to synthesise ferrosilicon alloy.

KEY WORDS: ferrosilicon; reaction kinetics; reaction mechanism; waste plastic; bakelite.

1. Introduction

The production process of ferrosilicon involves carbothermal reduction of silica and iron oxide with carbon in an electric arc furnace,¹⁾ the primary reactant materials include quartz, hematite and coke/coal. The most common ferrosilicon alloy phases are Fe₃Si (Suessite or Gupeite), Fe₅Si₃ (Xifengite), FeSi₂ (Ferdasilite), FeSi (Fersilite). Ferrosilicon production uses up to 10.5 MWh of electrical energy per tonne of ferrosilicon due to endothermic nature of reduction process.²⁾ China is major producer of ferrosilicon alloy and this alloy is widely used in as an additive for silicon and as a deoxidising element in cast iron and steel making industries and foundries. The reactivity of the reduction material is important to achieve high silicon yield in the ferrosilicon alloy and attributed to the major cost in production system.³⁾ Typically coal, charcoal, coke, woodchips are widely used reduction materials in silicon industry. Wood chips originate from hardwood not only used as reductant but also to enhance the permeability of the charged material to achieve good gas flow. The complex structure of coal/coke contains network of pores which gives high surface area and have higher fixed Carbon. The choice of reduction material depends on the process, product and environmental considerations. The material must have properties to reach high Si yield, eliminate the chance of unwanted materials in product or emission like phosphorus, mercury *etc.* Besides general requirements, silicon monoxide (SiO) reactivity is

very important. The SiO reactivity is the ability of carbon, in the form of coke/coal, to react with SiO, and form SiC and CO. Studies were conducted to investigate the effect of reduction material properties on ferrosilicon alloy production.^{4,5)} Also, a number of studies have investigated reaction mechanism and kinetics for silica to SiC or silicon formation using conventional reduction materials.^{6–10)} However, limited studies are found to investigate reaction kinetics for ferrosilicon alloy synthesis. Therefore, a comparative study of reaction kinetics and mechanism of ferrosilicon alloy formation was conducted by measuring the off gases coming from the reduction reactions using graphite and waste Bakelite as reducing agent.

Bakelite is extensively used in electrical and heavy duty automotive parts, kitchenware, washing machine impeller *etc.* due to its high hardness, strength, electrical and thermal insulating properties.^{11,12)} Since, Bakelite cannot be remoulded; it is difficult to recycle and hence generally landfilled.

From our group, we reported kinetic studies of carbon composite pellets using graphite¹³⁾ and silica reduction studies using graphite-Bakelite blend.¹⁴⁾ Bakelite transformation as reductants for ferrosilicon alloy synthesis is also reported.¹⁵⁾

In this paper, a fundamental comparative study on reaction kinetics and mechanism of ferrosilicon alloy synthesis, using reagent grade material, graphite and waste plastic, Bakelite as reducing agent within 1 623 K to 1 823 K (1 350°C to 1 550°C) is reported. Influence of temperature on ferrosilicon synthesis is also reported. Infrared Gas Analyzer (IR) was used to determine off gas analysis

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coming from reduction reactions to determine the reaction kinetics. Reaction product was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis. It was observed that reaction rate is strongly dependent on the temperature and activation energy for graphite and Bakelite bearing pellet is 238.07 kJ/mol and 140.29 kJ/mol respectively. Lower activation energy using Bakelite creates the opportunity to use waste Bakelite as reducing agent at lower temperature compared to conventional carbon materials to synthesise ferrosilicon alloy.

2. Experimental

Spherical pellets (2 gm, 10–12 mm in diameter) were made with silica (SiO_2) powder (0.5–10 μm , 99%), iron oxide (Fe_2O_3) powder (< 5 μm , $\geq$ 99%) and synthetic graphite (C) powder (< 20 μm)/Bakelite (125 μm). Generally, as particle size decreases, the rate of reduction reaction increases. Although, size of Bakelite particle (125 μm) is higher than graphite (20 μm), in this study higher reduction rate was observed for Bakelite. Required amount of carbon was measured from molar ratio of the stoichiometric reactions to produce ferrosilicon (reactions (1), (2)).¹⁶ Therefore, weight ratio of synthetic graphite (~100% C) containing pellets was SiO_2 : C (synthetic graphite): Fe_2O_3 (1:0.62:1). Bakelite containing pellets were made with weight ratio SiO_2 : C (Bakelite): Fe_2O_3 as 1:0.46:1 taking into account that %C in Bakelite char is 73.16%.¹⁶ Pellet preparation method used in the present study was identical to previous studies.^{16–18} To remove any moisture content, pellets were dried for 24 hours at $\sim 90^\circ\text{C}$. Chemical analysis of Bakelite is shown in **Tables 1(a)** and **1(b)**.

A schematic of the experimental set-up is in **Fig. 1**. A

Table 1. (a). Chemical composition of Bakelite. (b). Composition of Ash analysis of Bakelite.

(a)			
Composition (wt%)			
Ultimate Analysis		Proximate Analysis	
Total carbon	53.4	Fixed Carbon	31.70
Oxygen	11.6	Volatiles	47.55
Hydrogen	4.0	Moisture	3.01
Sulphur	0.017	Ash	17.74
(b)			
Compound	CaO	SiO_2	SO_3
wt%	94.53	5.14	0.33

Fig. 1. Schematic diagram of experimental set-up.

horizontal tube furnace equipped with super kanthal heating elements was used for heat treatment of pellets from 1 623 K to 1 823 K (1 350°C to 1 550°C). High purity (> 99%) argon gas was flowing at 0.8 L/min through gas inlet. The tube was sealed with a rubber O-ring and grease in order to avoid contamination from atmosphere and off-gas leakage. Constant gas flow was controlled by a gas flowmeter at gas inlet. Inferred gas analyser, IR (ABB, Advanced Optima Series, AO2020) was connected at gas outlet to measure CO, CO_2 and CH_4 off gases coming from reduction reactions. Gas analysis data were taken three times and average was taken into account for calculations to ensure reproducibility. CO and CO_2 gas generation were used to determine reaction kinetics and cumulative volume of gases was measured to estimate reaction rate. Gas concentrations data ppm (parts per million) from IR gas analyzer were converted into moles using standard gas equation. Reaction product was analysed by XRD (PAN analytical Xpert Multipurpose MPD). Copper $K\alpha$ radiation of 45 kV and 40 mA was used as an X-ray source, under the step size of 0.026° with 1° slit and 10 mm mask. Phase identification was done by using Xpert High Score Plus software. Synthesised ferrosilicon was also confirmed by SEM (Hitachi 3400-I) and EDS (Bruker X flash 5010) analysis.

3. Results and Discussion

Analyzing the reaction off-gas is an effective and dynamic method to determine the reaction controlling the reduction process. Therefore reaction kinetics and mechanism was determined by measuring off-gases released from the graphite and Bakelite bearing pellets. **Figure 2** is showing the generated gas concentration of graphite and Bakelite pellet. It was observed that CO gas was the dominant in off-gas release which was produced through the reduction reactions (reactions (1), (2)) for ferrosilicon synthesis.

Though CO gas release was comparatively high at initial stage in Bakelite pellet but released over a longer period of time in graphite pellet. Gases coming from the Bakelite degradation (CO and CH_4) enhanced the reduction reactions (reactions (3), (4)) initially therefore higher CO release was observed.

At 1 823 K (1 550°C), Bakelite generates significant amount of gases within 4 minutes and showed 69.47% carbon content in the solid residue.¹⁵ Concurrently, from XRD analysis of Bakelite char, it was observed that crystalline nature of Bakelite derived carbon was becoming more evident after 4 minutes onwards (**Fig. 3**) and that carbon started to reduce oxides, therefore the highlighted neck (Orange circle in **Fig. 2**) in Bakelite pellet can be attributed to the transition from gas phase to solid phase reduction reactions. Afterwards, as the supply of Bakelite derived

Fig. 2. Generated gas concentration from graphite and Bakelite pellet at temperature 1 823 K (1 550°C) during synthesis of ferrosilicon.

Fig. 3. XRD analysis of Bakelite chars at temperature 1 823 K (1 550°C).

carbon was used up and was lower than the graphite, the reactions reached almost completion before graphite pellet. CO_2 which is the main source of greenhouse gas was lower in Bakelite pellet compared to graphite pellet.¹⁵⁾ Graphite pellet did not show any trace of CH_4 gas, whereas Bakelite showed small amount of CH_4 due to degradation of Bakelite and a major portion of CH_4 gas helped reduction reactions (reaction (4)).^{14,19)}

Figure 4 compares the total amount of oxygen removal with time temperature of 1 623 K, 1 723 K and 1 823 K (1 350°C, 1 450°C, 1 550°C) due to the reactions occurring within the graphite and Bakelite bearing pellet. Total cumulative oxygen was measured from the ppm values of CO and CO_2 evolved during the reduction reactions by graphite and Bakelite. An almost linear increase in the initial stage followed by limiting values of cumulative oxygen removal was observed in all temperatures for both graphite and Bakelite bearing pellets as reactants are exhausted. It can be also observed that reduction reactions to synthesise ferrosilicon using graphite and Bakelite are temperature dependent which is found in previous studies²⁰⁾ as well. Extent of reduction can be improved by increasing temperature. However, Bakelite pellet showed lower dependency on temperature compared to graphite. At 1 623 K (1 350°C) and 1 723 K (1 450°C) Bakelite pellet showed almost same amount of

Fig. 4. Cumulative oxygen removal from graphite and Bakelite pellet at different temperature during synthesis of ferrosilicon.

oxygen removal and at 1 823 K (1 550°C) Bakelite pellet showed gradual increase in oxygen removal. This behavior of Bakelite can be attributed to the reactivity of Bakelite at lower temperature due to initial gas release from Bakelite degradation and less crystalline nature of Bakelite derived carbon compared to graphite. Alternatively graphite pellet showed almost double amount of oxygen removal from 1 623 K to 1 823 K (1 350°C to 1 550°C) temperature. At 1 823 K (1 550°C) both graphite and Bakelite pellet showed flat limiting values at the end however at 1 623 K (1 350°C) and 1 723 K (1 450°C) within 15 minutes (1 500 sec) it showed gradual increase which refers that at lower temperature reduction rate become slower therefore requires more time to reach the equilibrium condition.

The overall reduction is divided into three stages considering the slope of the curve of cumulative oxygen removal or reduction extent over time. Reduction extent was measured using Eq. (1). **Figure 5** is showing the reduction extent for graphite and Bakelite pellet at 1 823 K (1 550°C) with graphical representation. Stages in pellet reactions were

compared and determined on change in slope of the curve in reduction extent over time plot (Fig. 5) and in $\ln(P_{\text{CO}}/P_{\text{CO}_2})$ over time plot, shown in **Fig. 8**. At stage 1(0–120 sec), linear and sharp increase in reduction reaction is observed, due to Fe_2O_3 reduction and initial SiO_2 reduction¹⁵⁾ and graphically showed size reduction. Reduction product was confirmed by the XRD and EDS analysis as shown in **Figs. 6 and 7**.

$$\text{Reduction Extent}(X) = \frac{\text{initial mole of removable oxygen present in sample}(n_0) - \text{mole of oxygen remaining in the sample}(n_t)}{\text{initial mole of removable oxygen present in sample}(n_0)} * 100 \quad (1)$$

In stage 2 (120 sec–900 sec), most of reduction reactions occurred, and is divided into two regions. In stage 2-I, a steady state reaction region was observed which was followed by stage 2-II, where a slowing down of reactions occurred due to the formation of final product (ferrosilicon) and slag (SiC , $\text{CaSiO}_3/\text{Ca}_2\text{SiO}_4$) through reduction (Fig. 6). In-situ image also showed nucleation of metal droplets and slag phase. In stage 3, reactions reached almost completion

Fig. 5. Reduction extent for the graphite and Bakelite pellet at 1 823 K (1 550°C) during synthesis of ferrosilicon.

Fig. 6. Comparison of XRD analysis of Graphite and Bakelite pellet at 1 823 K (1 550°C) during synthesis of ferrosilicon.

Fig. 7. SEM and EDS analysis of ferrosilicon alloy synthesised by Graphite and Bakelite.

and therefore the reduction extent curve become steady and distinctively it showed metal and slag phases. Overall, graphite pellet showed complete reduction (100%) through formation of ferrosilicon as product and SiC in slag. Alternatively, formation of viscous slag $\text{CaSiO}_3/\text{CaSiO}_4$ in Bakelite pellet and lower amount of Bakelite derived carbon can be attributed to the comparatively lower reduction extent (~92%) and preceding steady state than graphite pellet. However, Bakelite pellet showed enhanced extent of reaction up to ~600 sec (stage 2) which can be observed from the gradient of the curves of graphite and Bakelite in Fig. 5.

Formation of ferrosilicon was confirmed by the SEM and EDS analysis shown in Fig. 7, where only Fe and Si peak was detected with low intensity carbon peak. Brighter phase in SEM image represents the higher iron concentration and darker phase represents the higher silicon concentration.

Figure 8 is showing $f=kt$ and $-\ln(1-X)=kt$ plot of graphite and Bakelite pellet over time to determine the possible controlling mechanism in each stage of the reduction process. In stage 1, though graphite and Bakelite pellet showed linearity differently, in both case, X and $-\ln(1-X)$, the slopes are nearly linear which implies that the rate is not controlled by one single mechanism, but a mixed control of possibly, mass transfer and chemical kinetics.²¹⁾ However in Stage 2 I and II, the curve shows better linearity when plotted with $-\ln(1-X)$, which indicate that the reaction mechanism is predominantly controlled chemically.²¹⁾ This is also in agreement with the XRD results (Fig. 6), where it was observed that formation of Fe_5Si_3 , FeSi , SiC , CaSiO_3 phase occurred within this stage (120 to 900 seconds) through chemical reactions.

It is first necessary to find the reaction at equilibrium to

determine which reactions are controlling in the system.²²⁾ A given reaction is at equilibrium when the off-gas $P_{\text{CO}}/P_{\text{CO}_2}$ concentration falls on the equilibrium $P_{\text{CO}}/P_{\text{CO}_2}$ value for that reaction.²²⁾ From literature it is evident that indirect reduction by CO is dominant in iron oxide reduction (reaction (5)) instead of direct reduction by carbon.^{13,23)} The two major intermediate products, SiC and SiO formation is also known to occur through gas phase reduction by CO in silica reduction (reactions (3), (7)).²⁴⁾ And Boudouard reaction (reaction (6)) exists at temperature above 1 273 K (1 000°C) and plays a vital role both iron oxide and silica reduction studies.^{24,25)} Therefore these reactions are considered to plot $\ln(P_{\text{CO}}/P_{\text{CO}_2})$ plot though ferrosilicon production involves a number chemical reactions including silica reduction and iron oxide reduction.

Figure 9 is showing the oxygen potential of the reaction off-gas which was calculated in terms of $P_{\text{CO}}/P_{\text{CO}_2}$ and compared with equilibrium $P_{\text{CO}}/P_{\text{CO}_2}$ of the individual reactions. From the graph it can be observed that stage 1, is mostly controlled by iron oxide reduction ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$), while stage 2-I is controlled by SiO formation and Boudouard reaction for both graphite and Bakelite bearing pellet. In stage 2-II and stage 3, $\ln(P_{\text{CO}}/P_{\text{CO}_2})$ concentration of Bakelite pellet shows that Boudouard reaction is at equilibrium, therefore SiO and SiC formation through

Fig. 8. Reduction of graphite and Bakelite pellet at 1823 K (1550°C) during synthesis of ferrosilicon to determine various controlling mechanisms.

the gas phase reduction reactions of silica are the rate controlling reactions. Instead, in graphite pellet at stage 2-II, $\ln(P_{CO}/P_{CO_2})$ value located between mixed Boudouard and SiO formation reaction control. Therefore in graphite bearing pellet, Boudouard reaction is also attributed to the controlling reactions along with SiO formation in stage 2-II. At stage 3, graphite pellet showing equilibrium towards Boudouard reaction showing less control in the system. At stage 3 (~900 sec), reaction already completed and due to the formation of the reaction product like ferrosilicon and deposition of slag ($SiC/CaSiO_3$) by reduction, reaction was

retarded. Therefore, reduction extent also showed steady state (Fig. 5). In-situ images of pellets at different stages are shown in Fig. 10. In stage 2 we could visually distinguish the formation of ferrosilicon alloys through the reduction reaction which is in agreement with the previous discussion. In-situ images at stage 3 also showed that the reduction became stable and synthesized metal droplets of ferrosilicon alloy was distinguishable from slag.

Temperature is an important factor that influences the rate of reactions. The dependency of reaction rate on temperature can be described by the activation energy, E_a defined

by Arrhenius equation. The activation energy represents the energy level that the reactant molecules must overcome to start the reaction to occur.

$$k = k_0 e^{-E_a/RT} \dots \dots \dots \text{reaction (8)}$$

Here, k is the rate constant derived from the plot of $-\ln(1-X)$ as function of time in stage 1 and 2 at temperature 1 623 K, 1 723 K and 1 823 K (1 350°C, 1 450°C and 1 550°C). A plot of $\ln(k)$ over $1/T$, is shown in **Fig. 11**, indicates the good linearity and yields an activation energy of 169.76 kJ/mol and 55.91 kJ/mol for graphite and Bakelite pellet for stage 1. For Stage 2, activation energy for graphite and Bakelite pellet is 238.07 kJ/mol and 140.29 kJ/mol respectively. It is noted that, activation energy for stage 1 and 2 for Bakelite pellet is lower than the graphite pellet. Initial gas generation from Bakelite, comparatively less crystalline nature of Bakelite derived carbon and less dependence on Boudouard reaction can be attributed to the lower activation energy. Moreover, both in graphite and Bakelite pellet activation energy is higher in stage 2 compared to stage 1. During stage 1, mostly iron oxide reduction was dominant and lower activation energy for iron oxide reduction can be attributed to the lower E_a value during stage 1. Reported activation energies of silica reduction are in the

range of 230 kJ/mol to 552 kJ/mol, depending primarily on the precursor silica and carbon sources, particle sizes, temperature ranges and the broad range of rate equation form which have been fit to the data.^{26,27} Also Filsinger and Bourrie⁹ reported activation energy within range of 305 kJ/mol to 505 kJ/mol within 1 683 K to 2 073 K (1 410°C to 1 800°C) temperature for specific silica reduction reaction which covers SiC, SiO and Si formation. The activation energies reported in this work are comparatively lower than the previously reported silica reduction studies. This study

Fig. 9. Measured and equilibrium $\ln(P_{CO}/P_{CO_2})$ values for the graphite and Bakelite pellet at 1 823 K (1 550°C) during synthesis of ferrosilicon.

Fig. 11. determination of activation energy of the graphite and Bakelite pellet at 1 823 K (1 550°C) during synthesis of ferrosilicon.

Fig. 10. In-situ images of graphite and Bakelite pellet at 1 823 K (1 550°C) during synthesis of ferrosilicon.

is not purely silica reduction as iron oxide was also used to produce ferrosilicon and reduction of iron oxide and solute iron could play the vital role to reduce the value of activation energy in the reaction mechanism.

As indicated in Fig. 11, the reaction with higher activation energy, E_a has a steeper slope; which represents that the reaction rate of graphite pellet is very sensitive to temperature change. This behavior is also in agreement with cumulative oxygen removal pattern (Fig. 4). In contrast, the reaction with a lower E_a is less sensitive to a temperature change. Therefore Bakelite pellet can be useful as a reductant even at moderately lower temperature to synthesise ferrosilicon alloy.

4. Conclusions

A fundamental comparative study on reaction kinetics and mechanism of ferrosilicon alloy synthesis, using reagent grade material, graphite and waste plastic, Bakelite as reducing agent is established. Off-gases evolving from reduction reactions were considered to determine the reaction rate and controlling mechanism. Based on present experiments, major conclusions are summarized as follows:

(1) Extent of reduction to synthesise ferrosilicon alloy by using either graphite or Bakelite as reductant, can be improved by increasing temperature. Though, Bakelite pellet showed lower dependency on temperature compared to graphite. Activation energy for graphite and Bakelite bearing pellet is 238.07 kJ/mol and 140.29 kJ/mol respectively.

(2) Stages (1 to 3) in pellet reactions were determined on change in slope in reduction extent over time curve and in $\ln(P_{CO}/P_{CO_2})$ over time curve. Stage 1 and 2I, was mostly controlled by iron oxide reduction followed by SiO formation and Boudouard reaction for both graphite and Bakelite bearing pellet. In stage 2-II, Bakelite pellet showed that Boudouard reaction reached at equilibrium, therefore SiO and SiC formation through the gas phase reduction reactions of silica are the rate controlling reactions. Instead, in graphite pellet at stage 2-II, showed mixed control of Boudouard and SiO formation reactions. At stage 3, reaction already completed and due to the formation of the reaction product like ferrosilicon and deposition of slag ($SiC/CaSiO_3$) by reduction, reaction was retarded for both graphite and Bakelite bearing pellet.

(3) The overall reduction mechanism was predominantly controlled by chemical reactions with both the reducing agent. Initially Bakelite bearing pellet showed faster reaction rate compared to graphite due to volatiles genera-

tion and less crystalline nature of Bakelite derived carbon.

(4) This comparative study will create new opportunities to use waste Bakelite as a reducing agent at lower temperature compared to conventional carbon materials to synthesise ferrosilicon alloy.

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