Influence of recycled wastes on ferrosilicon production in steel making applications: A short review

Anis Nadhirah Ismail¹, Mohd Hakim Ibrahim², Rita Mohd Said¹, Flora Somidin¹ and Syarifah Aminah Ismail²

¹Center of Excellence Geopolymer & Green Technology (CeGeoTech), Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis (UniMAP), Taman Muhibbah, 02600 Jejawi, Perlis, Malaysia
²Mineral Research Centre, Department of Mineral and Geoscience, Jalan Sultan Azlan Shah 31400 Ipoh, Perak, Malaysia.

Abstract. The potential transforming the waste materials into an alternative source was found in iron and steelmaking application that also would solved the world’s most problematic waste stream. Generally, converting the waste materials into auxiliary source only is accessible to certain wastes industries due to its difficulty to recycle hence generally landfilled. Recycling waste materials used in ferrosilicon production as carbon and silica source to control the reduction reaction with iron oxide. The present paper reviews the phase transformation and morphology in the production of ferrosilicon at temperature 1550˚C on graphite and plastic waste (bakelite) as the potential carbon materials and silica powder and glass waste (automotive glass - windshield, window glass) as alternatives silica source in production of ferrosilicon. The utilization of carbon material from plastic waste and silica source from glass waste (automotive glass) can be used for ferrosilicon synthesis and CO gas concentration comparable with conventional carbon source (graphite) typical silica source (silica powder). The utilization of recycled wasted is efficient due to enhancement in the reaction with iron oxide thus potentially replacing the conventional materials in ferrosilicon synthesis as well as minimizing the landfill wastes.

1 Introduction

Ferrosilicon (FeSi) production process is a carbothermic reduction process that used carbon material as reducing agent [1, 2]. In steelmaking industry, the type of carbon and silica source used in the ferrosilicon production have a significantly effect on the cost, energy consumption and stability of the operation [3]. An innovative approach based on recycling waste glass, plastic waste and agricultural waste has been reported by several researchers with aim to maximize use of waste resources for production of ferrosilicon [1, 3-8]. Farzana et al. (2014) reported that plastic waste from bakelite mainly used in kitchenwares, toys, electronic devices such telephones and radios, washing machines and etc. However, these wastes are being abundances due to its characteristic that cannot be remoulded thus problematic to be recycled. The bekelite going through the pyrolysis in order to develop resultant energy associated with less porous and uniformly carbon structure that can be used as carbon source in steelmaking [7].

Other flexible and resourceful material that can be used in multifaceted application is waste glass. Waste glass such windshield and window glass from automotive sector destined to landfill due to difficulty and costly processes. Waste glass can be used in ceramic production [9], as construction material [10] and for silicon production [11]. This provides an opportunity for industry to become a competitive price by converting the automotive waste glass as an auxiliary silica source.

In ferrosilicon production, the reduction of iron oxide followed the reaction in Eq. 1 and the Boudouard reaction in Eq. 2 occurred. The CO (carbon monoxide) released from iron oxide reduction process (Eq 1) facilitates the gas

Corresponding author: anisnadhirah@unimap.edu.my
phase reduction of silica through intermediate phase of SiO (Eq. 3 and 4). At higher temperature, the reduction of silica takes place by carbon. The silica was completely volatilized and gets vaporized at high temperature reaction [3, 5]. The reaction in silica and carbon materials initiates the contact point between SiO$_2$ and C. Once both SiO and CO are formed (Eq. 2 and 3), the reaction proceeds at the surface of carbon and silica particles through gas phase. Some amount of SiO will be used in the system and the remains will escape in the gas phase. Some amount of reduced silica in form of silicon (Eq. 4) dissolved into molten iron to form ferrosilicon while the remains were reduced to SiC (Eq. 5).

\[
\begin{align*}
Fe_2O_3(sol) + 3C(sol) & \rightarrow 2Fe(liq) + 3CO(gas) \\
C(sol) + CO_2(gas) & \rightarrow 2CO(gas) \\
SiO_2(sol) + CO(gas) & \rightarrow SiO(gas) + CO_2(gas) \\
SiO_2(sol) + C(sol) & \rightarrow Si(liq) + CO(gas) \\
SiO_2(gas) + 3C(sol) & \rightarrow SiC(sol) + 2CO(gas)
\end{align*}
\]

The typical ferrosilicon and silicon carbide are produced from direct reduction between typical silica (silica source) and coke (carbon source). Previous researchers by Sahajwalla et. al (2003) and Boonyaratchinda et al. (2020) stated that the reduction is a strong endothermic reaction that operating at high temperatures (2000 – 2500°C) thus attributed to high electrical energy requirement [12, 13]. The fundamental understanding of waste glass and plastic waste on ferrosilicon production in terms of phase transformation at different reduction time and off gas evolution during the reduction reaction at reduction temperature 1550°C are reviewed in this paper.

2 Raw Materials

In general, the raw materials used to produce ferrosilicon were graphite (conventional material, C: 99%) and bakelite (plastic waste, C: 53.4%) as carbon materials while silica powder (typical silica, SiO$_2$: 99%) and automotive glass (glass waste – windshield, SiO$_2$: 71% and window glass, SiO$_2$: 69.21%) as silica source [5, 6, 8]. The elemental analysis of the graphite and bakelite conducted using X-ray diffraction as shown in Table 1. It has been reported that XRD pattern of graphite showed mainly carbon with small amount of silica impurity pattern [8]. While, for the bakelite showed in Table 1 was dominated by the calcium carbonate with small amount of silica impurities were detected in the XRD pattern [6]. The reactions undergo between iron oxide, Fe$_2$O$_3$ (99%) with two different carbon materials and two types of silica source.

| Carbon materials | Graphite | Bakelite |
|-----------------|---------|----------|
| Phase           | C, SiO$_2$ | CaCO$_3$, SiO$_2$, CaO |

3 Ferrosilicon Synthesis

In ferrosilicon synthesis, the waste glass and carbon materials are usually ground to powder. The waste glass, carbon material and iron oxide then placed in a glass jar and mixed and form into spherical shape. The reduction reactions done by previous researchers were conducted at 1550°C in horizontal tube furnace under Argon gas atmosphere with flowrate 1 L/min within 2, 4, 8 and 15 minutes reaction time. The schematic of the experimental arrangement presented in Figure 1. In order to measure the gas evolved during the reduction, an IR gas analyser was coupled to the furnace [4]. The reduced ferrosilicon samples were analysed by X-ray diffractometer.
Fig. 1. Schematic representation of the experimental arrangement.

4 Phase Transformation

The phase transformation of the reduced pellets of silica/graphite, silica/bakelite, automotive glass/bakelite and automotive glass/graphite/bakelite at 1550°C as reported by several researchers are shown in Table 2. XRD of the overall reduced pellets showed the formation of ferrosilicon (15 min). In silica/graphite reduced pellet, it was reported that the formation of SiC, FeSi and FeSi$_2$ were predominantly after 15 min reduction time [4]. The appearance of SiC may cause by the solid phase reaction between high content of silica in silica powder (99%) and high content of carbon in graphite (99%) during the reduction process [6]. According to previous research stated that the formation of iron silicon (FeSi and FeSi$_2$) in reduced pellet was due to the gas phase reaction of silica with the iron oxide [13]. For the silica/bakelite reduced pellet, peak of Fe$_5$Si$_3$, CaSiO$_3$/Ca$_2$SiO$_4$ and FeSi were majorly detected in XRD pattern after 15 min of reduction time [4]. Boonyaratchinda and Kongkarat (2020) reported that the appearance CaSiO$_3$/Ca$_2$SiO$_4$ was probably occurred during the reaction between CaCO$_3$/CaO and silica. During the smelting process, CaSiO$_3$/Ca$_2$SiO$_4$ covers the liquid molten steel surface avoiding the heat loss [14]. Compared to silica/graphite, in within 8 – 15 min, the formation of ferrosilicon by graphite (FeSi, FeSi$_2$) is in a greater level of silicon compared to bakelite (Fe$_5$Si$_3$, FeSi) [1, 6]. High crystalline graphite drives the rapid carbon dissolution in iron and lead to increase the rate of ferrosilicon formation [7].

While, the XRD analysis of automotive glass/bakelite reduced pellet at beginning of reaction (2 min) it was reported that the iron phase was detected along with solute carbon and unreacted silica. The Fe$_3$Si phase starts to appear at 4 min reaction time and become sharper until 15 min reduction time due to the distinguished from the slag [1]. Compared to XRD analysis of automotive/graphite/bakelite reduced pellet, various phases detected at the end of the reduction and predominantly by Fe$_3$Si$_3$ and SiC phase as presented in Table 2. Utilization of graphite/bakelite as carbon material elucidating that the reduction of iron oxide is much easier than the reduction of silica according to the formation of Fe$_3$Si within 2 min [5, 15]. As the reduction proceed, the reduction of silica into silicon become favoured and the structural composition of ferrosilicon changes from Fe$_3$Si to Fe$_5$Si$_3$ indicating the increasing of silicon content in ferrosilicon [6].

Table 2. XRD analysis of silica/graphite, silica/bakelite, automotive glass/bakelite and automotive glass/graphite/bakelite after reduction time at 2, 4, 8 and 15 minutes at 1550°C [1, 4, 6]

| Reduction time | 2 minutes | 4 minutes | 8 minutes | 15 minutes |
|----------------|-----------|-----------|-----------|------------|
| Silica/graphite | SiO$_2$, C, FeSi | FeSi, SiO$_2$, Fe/Si, C | FeSi, SiC, SiO$_2$, C | SiC, FeSi, FeSi$_2$, SiO$_2$ |
| Silica/bakelite | SiO$_2$, FeSi, C | FeSi, SiC, SiO$_2$, C | FeSi, CaSiO$_3$/Ca$_2$SiO$_4$, FeSi, SiC, SiO$_2$ | FeSi, CaSiO$_3$/Ca$_2$SiO$_4$, FeSi, SiC |
| Automotive glass/bakelite | Fe, SiO$_2$, C, CFe$_{15.1}$ | Fe, Si, C | FeSi | FeSi |
| Automotive glass/graphite/bakelite | Fe, Si, C, SiO$_2$ | SiC, FeSi, C | FeSi, SiC, C | FeSi, SiC, C, SiO$_2$ |
5 CO Gas Concentrations

The gas released during the reduction process also play a major role in silica/ graphite, silica/ bakelite, automotive glass/ bakelite and automotive/ graphite/ bakelite in silica reduction. Table 3 shows the CO gas concentration released during the reduction reported by several researchers [1, 4, 6]. The CO gas released of the overall reduced pellets was dominated by CO gas that was produced during the reduction reaction (Eq. 1, 4 and 5) for ferrosilicon synthesis. Based on the Table 3, the CO gas released by silica/ bakelite (0.0012 moles at 1 min) was comparatively high compare to others followed by silica/graphite (0.0011 moles at 1.5 mins), automotive glass/ bakelite (0.0010 at 1.3 mins) and automotive glass/ graphite/ bakelite (0.0007 moles at 1 min). However, the utilization of graphite as carbon materials [4, 6] was found that the CO gas release over a longer time compared to bakelite [1, 4] as the steady period was achieved at 18 and 12 mins for silica/graphite and automotive glass/graphite/Bakelite respectively while steady period was achieved at 9 mins for silica/ bakelite and automotive glass/ bakelite.

At initial stage of reduction, gases from volatilization and degradation of bakelite enhance the reduction reaction therefore higher CO generated was observed. As the process proceed, the carbon content of bakelite was used up and become lower than graphite that contained high carbon content, the reactions of bakelite reached to the almost completion before the graphite one. XRD analysis also showed the production of ferrosilicon at the beginning of reduction (2 – 4 min) due to the fast rate of reduction reaction according to higher CO gas released when bakelite was used as carbon materials (Table 3). For the automotive glass/ graphite/ bakelite, the carbon materials of bakelite contribute at the beginning of the reduction while graphite reacted steadily until the end of the reduction since the CO concentration started to increase again at 3 mins reaction time then slowly decrease at 5 min reaction time [6]. The formation and the structural composition changes of ferrosilicon can be observed with longer reduction time.

Table 3. Generated CO gas concentration from (a) silica/ graphite, (b) silica/ bakelite, (c) automotive glass/ bakelite and automotive glass/ graphite/ bakelite after reduction at 1550ºC [1, 4, 6]

| Samples                        | Maximum CO released | Reaction completion          |
|--------------------------------|---------------------|------------------------------|
|                                | Time                | Moles                        |                               |
| Silica/ graphite               | At 1.5 minutes      | 0.0011                       | Steadily at 18 minutes        |
| Silica/ bakelite               | At 1 minute         | 0.0012                       | Steadily at 9 minutes         |
| Automotive glass/ bakelite     | At 1.3 minutes      | 0.0010                       | Steadily at 9 minutes         |
| Automotive glass/ graphite/ bakelite | At 1 minute   | 0.0007                       | Steadily at 12 minutes        |

6 Conclusions

In conclusion, the ferrosilicon phases can be developed during the reduction reaction at 1550ºC within 15 min reaction time using graphite (conventional material) and bakelite (plastic waste) as carbon materials and silica powder (typical silica) and automotive glass (glass waste) as silica sources. The formation of ferrosilicon at early reduction time indicates high CO gas can be released by volatilization and degradation processes of bakelite at initial stage that resulted to faster reduction reaction. However, high carbon content in graphite leads to the CO gas releases over a longer period drives to steady reduction reaction. Moreover, the utilization of carbon material from plastic waste and silica source from glass waste (automotive glass) has the potential to be used for ferrosilicon synthesis. Thus, a sustainable ferrosilicon production process with new carbon source and silica source is more preferable.
References

1. R. Farzana, R. Rajarao, V. Sahajwalla, Materials Letters 116, 3 (2014)
2. M. Tangstad, J.O Beukes, J. Steenkamp, E. Ringdalen, New trends in Coal Conversion, Coal - Based Reducing Agents in Ferroalloys and Silicon Production, 34 (2019)
3. N.F.M. Yunos, M.A. Idris, S.R.R Munusamy, K. Perumal, IOP Conf. Series: Materials and Engineering 975, 7 (2020)
4. R. Farzana, R. Rajarao, V. Sahajwalla, ISIJ International 57, 8 (2017)
5. R. Farzana, R. Rajarao, V. Sahajwalla, Waste management & Research 34, 9 (2016)
6. R. Farzana, V. Sahajwalla, Novel Recycling to Transform Automotive Waste Glass and Plastics into SiC-Bearing Resource by Silica Reduction, Journal of Sustainable Metallurgy 1, 10 (2015)
7. R. Farzana, R. Rajarao, V. Sahajwalla, Industrial & Engineering Chemical Research 53, 8 (2014)
8. R. Farzana, V. Sahajwalla, The Minerals. Metals & Materials Society, 10 (2013)
9. S.R. Braganca, J. Vicenzi, K. Guerino, C.P. Bergmann, Waste Management & Research 24, 7 (2006)
10. J.L. Calmona, A.S. Sauera, G.L. Vieiraa, J.E.S.L. Teixeira, 53, 9 (2014)
11. M. Ogura, I. Astuti, T. Yoshikawa, K. Morita, H. Takahashi, Industrial & Engineering Chemical Research 43, 4 (2004)
12. V. Sahajwalla, C. Wu, R. Khanna, N.S. Chaudhury, J. Spink, ISIJ International 43, 7 (2003)
13. M. Boonyaratitchinda, S. Kongkarat, Materials Science Forum 977, 7 (2020)
14. V. Dosaj, M. Kroupa, R. Bittar, Kirk-Othmer Encyclopedia of Chemical Technology 0, 25 (2005)
15. F. McCarthy, V. Sahajwalla, J. Hart, N. Saha-Chaudhury, Metallurgy Material Trans B 34, 8 (2003)