Article

Synthesis of Ferroalloys via Mill Scale-Dross-Graphite Interaction: Implication for Industrial Wastes Upcycling

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Abstract: Mill scale and aluminum dross are the industrial wastes from steel and aluminum industries, which have high concentrations of FeO and Al2O3, respectively. This paper reports the conversion of reducible metal oxides in scale and dross into an alloy via carbothermic reduction at 1550 °C. Scale and dross were mixed with graphite into three different C/O molar ratios of 1, 1.5, and 2 to produce a pellet. The pellets were heated at 1550 °C for up to 6 h under an argon atmosphere. By this method, carbothermic reductions were found to proceed and formed Fe–Si–Al–C alloy that consists of FeAl and FeSi phases. The presence of Si in the alloy came from the reduction of SiO2 in aluminum dross. Levels of Al and Si in the alloy increase with increasing C/O molar ratios. However, the Si level in the alloy was found to stabilize since 3 h, while the Al level increases with increasing time up to 6 h. Unreacted oxides in the wastes had an insignificant effect on the ferroalloy formation. These results provide evidence for carbothermic reduction of the FeO–Al2O3–SiO2 system at 1550 °C and show the novel method to upcycling aluminum dross and mill scale toward a circular economy.

Keywords: industrial wastes; mill scale; aluminum dross; ferroalloys

1. Introduction

The industrial sector had been developed and expanded rapidly in recent decades, leading to the generation of waste. Steel and aluminum making are heavy industries that produce tremendous amounts of waste and by-products, such as slag, dust, mill scale, and dross. Mill scale is categorized as a by-product, generated from the hot rolling of semi-finished steel products, such as slab, bloom, and billet. Mill scale contains >70 wt% of metallic iron or >90 wt% of iron oxides, and thus it had been widely interested in many applications [1–10]. It was found to be recycled in the smelting process by mixing with coal or coke and used as a charge material to replace iron ore or scrap iron [1,2]. The direct reduction of mill scale had also been investigated using several reducing agents, such as biomass [3,4] and reducing gas [5,6]. The obtained products from the direct reduction of mill scale were iron powder and iron-bearing compound [7–10]. Aluminum dross is a by-product of the aluminum industry. It is generated during the aluminum melting process. The dross is mostly re-melted to extract the metallic aluminum using a rotary kiln. Aluminum dross generated after the re-melted process is secondary dross, which mainly comprises Al2O3 and salts [11]. It was mostly buried or landfilled causing soil and groundwater pollution. Aluminum dross is reactive with water which can generate various gaseous species, such as NH3, CH4, and H2S [12]. Thus, it is considered hazardous industrial waste, and the movement or transfer of the waste needs to comply with the Basel Convention [13]. The deposal of dross is a high cost for aluminum melting industries. Therefore, a good management method is needed for the tremendous increase in the volume of industrial waste. Aluminum dross had been utilized via several processes and can be classified into wet, dry, and without process [14–24]. The wet process was carried out using
acid and base leaching for Al recovery [15], absorbent/catalyst [16,17], and alumina [18,19] productions. The dry process was conducted by heating at a temperature above 1000 °C for the production of composite [20], refractory [21], and hercynite [22]. Aluminum dross can also utilize directly without processing for the production of geopolymers [23] and filler [24].

Synthesis of various metals using wastes and non-waste materials had been reported previously [25–32]. Jamieson et al. [25] separated red sand into a high iron oxides fraction, silica, and a mixture of iron and silica by using low and high magnetic separators. Zhu et al. [26] reported the extracting of various metals from red mud using acid leaching, solvent extraction, polymerization process, alkali leaching with pressure, and the aging process. Jadhav and Hocheng [27] have reported on extracting metals from several types of wastes using sulfuric/citrus/oxalic acids and microbiological leachants. Wei et al. [28] utilized silicon cutting waste (SCW) from the diamond wire sawing process by mixing it with aluminum powder and heated at temperatures of 1000–1500 °C. The production of Al–Si alloys can be synthesized by a one-step smelting process [28]. Khanna et al. [29] have reported on recovering multiple metals from various industrial wastes including fly ashes, red mud, mill scales, water treatment residues, and biomass. Carbothermic reduction of Al2O3:Fe2O3:C and Al2O3:Fe2O3:SiO2:C systems at the temperatures of 1450–1700 °C for up to 2 h had been widely studied. The reduction of FeO: and SiO2: was observed at 1450 °C, leading to the formation of Fe–Si–C alloys, while the reduction of Al2O3: was seen to start at 1550 °C and complete at 1600–1700 °C [29]. Synthesis of ferrosilicon alloys from rice husk and rubber tree bark had also been reported [30,31]. Boonyaratchinda et al. [31] employed rice husk as a silica source and rubber tree bark as a carbon source for the recovery of ferroalloy. By this, the Fe–Si alloy was observed from a carbothermic reduction in the SiO2:Fe2O3:C system at 1550 °C after 30 min of interaction with Si content in the ferrosilicon alloy of 45.32 wt% [31].

Khanna et al. [32] investigated interaction of Al2O3:C–Fe system at 1550 °C under inert argon atmosphere using pure alumina, graphite and a piece of steel. Carbothermic reduction reaction of Al2O3 by carbon in the presence of liquid steel was observed. The formation of Fe–Al–C ferroalloys was reported for the system of Al2O3:22.82 %C substrate interacted with a piece of Fe (0.6 %C). In this system, alumina fibrous was observed after 2–3 h of reaction and then the Fe–Al–C ferroalloy was formed after 5.5 h and completely transformed after 6 h. The synthesized Fe-Al-C ferroalloy composes of a metallic Fe:Al phase along with a carbon phase in the form of graphite flake. The presence of liquid steel in the system acts as a metallic solvent to trap the reduced Al in the system [32]. These studies on extracting or recovering metal from waste, non-waste, and industrial byproducts are still to a moderate extent [25–32]. Some of these used several steps and/or high temperatures to extract the metals, and thus have a small or moderate economic worthiness.

Aluminum dross and mill scale contain high amounts of Al2O3 and FeO2, respectively. The utilization of aluminum dross as a source of alumina for extracting Al had not been reported previously. Therefore, it is quite new to extract Al and the other metal from aluminum dross, which could be one of the novel management methods rather than buried or landfill. The present study aims to evaluate the possibility of utilizing aluminum dross and mill scale as a source of Al2O3 and FeO2 to synthesize ferroalloys at 1550 °C. The carbothermic reduction reaction of the FeO2:Al2O3:C system will be investigated. The influence of carbon content in the system and interaction times will be reported and investigated.
2. Materials and Methods

2.1. Sample Preparation

2.1.1. Aluminum Dross

Aluminum dross used in the present study was supported by TOP Five manufacturing, the aluminum melting industries located in the eastern province of Thailand. The dross was sieved into a powder of <180 μm. XRF analysis of aluminum dross is presented in Table 1, showing 69.94 wt% of Al2O3 and 5.01 wt% of SiO2 as the major components.

| Oxides (wt%) | Al2O3 | SiO2 | Fe2O3 | CaO | K2O | MgO | MnO | Na2O | SO3 | CuO | TiO2 | ZnO | Others |
|--------------|-------|------|-------|-----|-----|-----|-----|------|-----|-----|------|-----|--------|
|              | 69.94 | 5.01 | 0.54  | 1.0 | 0.76| 4.91| 0.15| 10.65| 2.46| 0.37| 0.17  | 0.25| 3.79   |

2.1.2. Mill Scale

Mill scale was collected from UMC Metal Co., Ltd., Chonburi, Thailand. The scale was ground in a ring mill and sieved into a powder of <180 μm. Table 2 shows XRF analysis of the mill scale used in this study, containing 93.66 wt% of Fe2O3 as the main components.

| Oxides (wt%) | Fe2O3 | SiO2 | Al2O3 | CaO | SO3 | TiO2 | K2O | P2O5 |
|--------------|-------|------|-------|-----|-----|------|-----|------|
|              | 93.66 | 1.42 | 0.82  | 0.17| 0.08| 0.04 | 0.02| 0.04 |

2.1.3. Pellet Preparation

Aluminum dross, mill scale, and graphite were blended homogeneously into three different C/O molar ratios using rolling mill, as shown in Table 3. C is the total moles of carbon from graphite in the blends, while O is total moles of oxygen from Al2O3 and Fe2O3 in the dross and mill scale, respectively. Graphite used in the experiments contains 98.5 wt% of carbon (Cat. No.17046-02) obtained from Kanto Chemical Co., Inc., Tokyo, Japan. Some water was added to the blends to make a spherical composite pellet with the weight of approximately 5 g. The pellets were dried in the oven at 90 °C for 48 h and used for high temperature experiments.

| Blend | Dross (wt%) | Scale (wt%) | Graphite (wt%) | C/O Ratios |
|-------|------------|-------------|----------------|-----------|
| A     | 41.34      | 48.44       | 10.21          | 1         |
| B     | 39.37      | 46.09       | 14.57          | 1.5       |
| C     | 37.52      | 43.95       | 18.53          | 2         |

2.2. High-Temperature Interactions

The overview of experimental procedures is given in Figure 1. The high-temperature interactions were investigated in a tube furnace. The pellet was put in a crucible and then inserted into the cold zone of the furnace for 5 min to prevent thermal shock. The crucible was then inserted into the hot zone where the temperature was 1550 °C for 1, 2, and 3 h. High-purity argon (99.99%) was purged into the tube furnace at the rate of 1 L/min at all times to prevent oxidation of the pellet. The quenched pellets were collected for further analysis.
2.3. Analysis

The pellets were mounted in the resin and cross-sectioned for SEM analysis. SEM and EDS analysis were used to observe the formation of ferroalloy and its compositions. Some of the quenched pellets were ground into powder for XRD analysis. XRD was employed to investigate the phases that occurred in the synthesized ferroalloys.

3. Results and Discussion

3.1. Carbothermic Reduction Reactions

Figure 2 shows the pellets after they were heated at 1550 °C as a function of times. The outer surface of the pellets was seen to crack and some of them were covered by white materials, which is fibrous alumina [32]. The presence of fibrous alumina on the pellets indicates the occurrence of a carbothermic reduction reaction of alumina [32]. The SEM micrograph of the cross-sectioned pellets is shown in Figure 3. The formation of metal droplets was observed as a white–grey phase and clearly separated from the unreacted oxides phase. These indicate the occurrence of carbothermic reduction reactions of Fe2O3 in mill scale, Al2O3, and SiO2 in aluminum dross at 1550 °C.
Figures 4–6 show XRD spectra of the pellets with C/O ratios of 1, 1.5, and 2 after heating at 1550 °C, respectively. XRD spectra confirmed that the synthesized alloys produced in the systems were iron aluminide (Fe₃Al) and iron silicide (Fe₃Si). The other phases were carbon and unreacted Al₂O₃ and SiO₂ remain in the system. Fe₃Al peak occurs at 2theta of approximately 43.4°, while the major peak of Fe₃Si occurs at 2theta of 44.8°. For the pellets with C/O = 1, intensity of Fe₃Al peak was higher than that of Fe₃Si peak, and this trend happened for 3 h of interaction. With increasing C/O ratios, the intensity of Fe₃Si peak was observed to increase and get stronger than that of Fe₃Al peak in the case of the pellet with C/O = 2.

Figure 3. SEM micrograph of cross-sectioned pellets after heating at 1550 °C for up to 3 h.

Figure 4. XRD patterns of the pellet (C/O = 1) after heating at 1550 °C for up to 3 h.
The formation of Fe₃Al and Fe₃Si can be explained via the carbothermic reduction reaction of Fe₂O₃, Al₂O₃, and SiO₂ at 1550 °C under an argon atmosphere. The reduction of Fe₂O₃ by solid carbon atom can occurred via Equations (1)–(3), and produce liquid Fe and CO into the system [32,33]. The produced CO could possibly react with Fe₂O₃ as a reducing agent and produce liquid Fe and CO₂ into the system, as shown in Equations (4)–(6) [32,33]. At 1550 °C, standard Gibbs free energy (ΔG°) for Equations (3) and (6) is −124.46 kJ and −272.71 kJ, respectively.

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

The overall carbothermic reduction of Al₂O₃ as shown in Equation (7), is known to occur at the temperature of over 2200 °C at 1 atm [34]. This reaction could produce Al₂O gas, Al vapor, and CO gas via the reaction pathway, Equations (8) and (9). However, the
reduction reaction of Al₂O₃ by solid carbon had also been reported to start at a temperature of 1450 °C with a small amount of Al vapor and gaseous species of AlO and Al₂O [35]. Equations (7)–(9) had also been reported to proceed at 1550 °C in the presence of metallic solvent [29,32,34]. Thus, the carbothermic reduction of Al₂O₃ in the present study could occur in the presence of liquid Fe as the metallic solvent.

\[
\begin{align*}
\text{Al}_2\text{O}_3(s) + 3\text{C}(s) &= 2\text{Al}(l) + 3\text{CO}(g) \quad (7) \\
\text{Al}_2\text{O}_3(s) + 2\text{C}(s) &= \text{Al}_2\text{O}_3(g) + 2\text{CO}(g) \quad (8) \\
\text{Al}_2\text{O}_3(g) + \text{C}(s) &= 2\text{Al}(g) + \text{CO}(g) \quad (9) \\
\text{SiO}_2(s) + \text{C}(s) &= \text{SiO}(g) + \text{CO}(g) \quad (10) \\
\text{SiO}_2(g) + 2\text{C}(s) &= \text{SiC}(s) + \text{CO}(g) \quad (11) \\
\text{SiO}(g) + \text{SiC}(s) &= 2\text{Si} + \text{CO}(g) \quad (12) \\
\text{SiO}(g) + 2\text{SiC}(s) &= 3\text{Si} + 2\text{CO}(g) \quad (13)
\end{align*}
\]

For SiO₂, the possible reaction could proceed through the reduction of SiO₂ into Si or SiC, as shown in Equations (10)–(13). The carbothermic reaction of SiO₂ has reaction rates at temperature above 1400 °C, and thus could occur at the experimental temperature of 1550 °C [29,30]. The carbothermic reduction reactions of Fe₂O₃, Al₂O₃, and SiO₂ at 1550 °C produce Fe, Al and Si into the system. The produced Al could have high affinity for liquid iron and thus transfer into liquid iron phase and form iron aluminide (Fe₃Al) [36], while Si could be removed from the reaction zone through dissolution into liquid iron phase and form iron silicide (Fe₃Si) [30]. During the presence of liquid iron, carbon dissolution into liquid steel could proceed due to the contact between liquid iron and solid carbon from graphite. Therefore, the final product was the Fe–Al–Si–C alloy.

3.2. Effect of Carbon

SEM and EDS analysis were employed for the metallic phase that obtained from the pellets of C/O ratios of 1, 1.5, and 2 after heating for 3 h, as shown in Figures 7–9. The composition of the ferroalloys was roughly determined using EDS analysis and given in Table 4. The metallic phase was found to be Fe–Al–Si–C alloys for all cases. For C/O = 1, the alloy composes of 0.69 at% of Al and 4.15 at% of Si with the others being iron and carbon. With increasing carbon to C/O = 1.5, Al and Si levels have increased to 7.30 and 9.94 at%, respectively. However, there was no further increase in Si level with increasing carbon to C/O = 2, while the Al level kept rising from 7.3 at% to 8.59 at%.

| Blend | C/O Ratios | Fe (%) | Al (%) | Si (%) | C (%) |
|-------|------------|--------|--------|--------|-------|
| A     | 1          | 69.32  | 0.69   | 4.15   | 25.84 |
| B     | 1.5        | 56.08  | 7.30   | 9.94   | 26.68 |
| C     | 2          | 48.19  | 8.59   | 8.29   | 34.93 |
Figure 7. SEM micrograph and EDS spectra of the cross-sectioned pellet (C/O = 1) after heating at 1550 °C for 3 h.

Figure 8. SEM micrograph and EDS spectra of the cross-sectioned pellet (C/O = 1.5) after heating at 1550 °C for 3 h.

Figure 9. SEM micrograph and EDS spectra of the cross-sectioned pellet (C/O = 2) after heating at 1550 °C for 3 h.
Figure 10 shows the variation of Al and Si concentration in the ferroalloy as a function of carbon content in the system (C/O ratios). It is clearly seen that the carbothermic reduction of SiO$_2$ precedes the reduction of Al$_2$O$_3$ when carbon content in the system has reached C/O = 1.5, and vice versa when increasing carbon to C/O = 2. These indicate that the reduction of SiO$_2$ can reach completion at 1550 ºC, and carbon content in the system of C/O > 1.5 is excessive. On the other hand, the reduction of Al$_2$O$_3$ still carries on and cannot achieve complete reduction at this state. The lower carbon in the system of C/O = 1 was likely to have an inadequate carbon atom for Al$_2$O$_3$ reduction. This is because carbon will be consumed for Fe$_2$O$_3$ reduction first and then SiO$_2$ reduction. The remaining carbon will be for Al$_2$O$_3$ reduction due to the lowest driving force of the reaction at 1550 ºC.

![Figure 10](image-url)

**Figure 10.** Comparison of elemental atomic percent in the synthesized metal after heating at 1550 ºC for 3 h.

3.3. Effect of Time

SEM and EDS techniques were used to analyze the metallic phase that obtained from the pellets of C/O = 2 after heating at 1550 ºC for 1, 2, 3 and 6 h, as shown in Figure 11. Composition of the alloy was EDS analyzed and given in Table 5. With high carbon concentration in the system, the carbothermic reduction of Al$_2$O$_3$ precedes the reduction of SiO$_2$ since 1 h of interaction. The level of Al in the alloy was 6.53 at% at 1 h and keep pace to reach 14.62 at% after 6 h, while Si level was 2.17 at% at 1 h and found to stabilize between 6–8 at% since 2 h until 6 h. These indicate the faster complete reduction of SiO$_2$ than that of Al$_2$O$_3$. 
Figure 11. Comparison of SEM micrograph and EDS spectra of the cross-sectioned pellet (C/O = 2) after heating at 1550 °C for 1, 2, 3, and 6 h.

| Heating Time (h) | Fe (at%) | Al (at%) | Si (at%) | C (at%) |
|------------------|----------|----------|----------|---------|
| 1                | 55.49    | 6.53     | 2.17     | 35.81   |
| 2                | 42.11    | 8.7      | 6.06     | 43.13   |
| 3                | 48.19    | 8.59     | 8.29     | 34.93   |
| 6                | 48.02    | 14.62    | 7.99     | 29.37   |

Table 5. Composition of the synthesis metals for the sample (C/O = 2).

Figure 12 shows the variation of Al and Si concentration in the ferroalloy as a function of time for the pellet with C/O = 2. It looked like the carbothermic reduction of Fe₂O₃,
Al₂O₃ and SiO₂ in this system had proceeded almost concurrently, but with different kinetic rates depending on the driving force for each reaction. This is because the excess carbon of C/O = 2 in the pellet, provide adequate carbon atom for the carbothermic reduction of each reducible oxide. Even though SiO₂ is known to proceed at a faster rate than Al₂O₃, Al concentration in the alloy was higher than Si because the higher amount of Al₂O₃ (69.94 wt%) in the dross compared to SiO₂ content (5.01 wt%).

For the synthesis of Fe–Al–Si–C alloys, carbon need to be provided adequately for each reducible oxide, such as C/O = 2. An interaction time of 3 h was more suitable than 6 h due to an economic point of view. Figure 13 shows the SEM micrograph and EDS elemental distribution in the bulk metal obtained from the pellets of C/O = 2 after heating at 1550 °C for 3 h. It can be observed that Al, Si, and C distribute over the entire Fe matrix. The present studies have shown that industrial wastes such as mill scale and aluminum dross can be successfully utilized or valorized as a source of Fe₂O₃, Al₂O₃, and SiO₂ for the synthesis of Fe–Al–Si–C alloys.

Figure 12. Comparison of elemental atomic percent in the synthesized metal from the pellet (C/O = 2) after heating at 1550 °C for 1, 2, 3, and 6 h.

Figure 13. SEM micrograph and EDS elemental contour of the cross-sectioned metal droplet obtained from pellet (C/O = 2) after heating at 1550 °C for 3 h.
4. Conclusions

Synthesis of ferroalloys at 1550 °C using a mill scale and aluminum dross as a source of metal oxides was successfully investigated. The experimental results can be concluded as below.

1. Carbothermic reduction reactions of FeO in mill scale, Al2O3, and SiO2 in aluminum dross can proceed at 1550 °C. The formation of metal droplets was observed and clearly separated from the unreacted-oxides phase. The synthesized alloys produced in the systems were Fe–Al–Si–C ferroalloys consisting of iron aluminide (Fe3Al) and iron silicide (FeSi) phases. Carbothermic reduction of Al2O3 in the present study can occur in the presence of liquid Fe as the metallic solvent.

2. For low carbon content in the system (C/O = 1), carbon was inadequate for Al2O3 reduction because it will be consumed by FeO reduction first and then SiO2 reduction. The remaining carbon will be for Al2O3 reduction due to its lowest driving force of the reaction at 1550 °C.

3. For high carbon content in the system (C/O = 2), it looked like the carbothermic reduction of FeO, Al2O3, and SiO2 in this system had occurred almost concurrently, but different kinetic rates depend on the driving force for each reaction. The excess carbon in the pellet will provide adequate carbon atoms for the carbothermic reduction of each reducible oxide.

4. Carbothermic reduction of SiO2 1550 °C can complete within 2–3 h, while a longer time is needed for the carbothermic reduction of Al2O3 to reach completion. However, the conditions of C/O = 2 and interaction time of 3 h were suitable for the synthesis of Fe-Al-Si-C due to the economic point of view. Further investigation is essential for the mechanical properties of the synthesized ferroalloys.

5. The innovation of this study was to extract Fe, Al, and Si from metal oxides bearing industrial wastes at temperatures as low as 1550 °C in one step process. The final product was in the form of Fe–Al–Si–C alloys. This research increases the possible methods for industrial waste management, decreases the negative effect on the environment, and enhances sustainability for materials processing toward a circular economy.

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