Effect of sulfur and sodium sulfate on phase transformation and microstructure on carbothermic reduction of Indonesian ilmenite

Agung Setiawan¹, Sri Harjanto¹

¹Department of Metallurgy and Materials Engineering
Faculty of Engineering, Universitas Indonesia, Kampus Baru UI Depok, 16424, Indonesia

*Corresponding author: agung.setiawan72@ui.ac.id

Abstract. Utilization of ilmenite and pulverized biomass of palm kernel shell is a beneficial solution to deal with the depletion of high-grade titanium minerals and manage of palm oil waste. The purposes of this research are to analysis the phase transformation and microstructure with additive addition. Sulfur and sodium sulfate have used an additive with an additional dosage of 0%, 1.5%, 3.0%, and 4.5%, and the reductant was the pulverized palm kernel shell biomass. The ilmenite concentrate was reduced at 1200 °C for 60 minutes in inert condition (N₂ atmosphere). Testing methods performed are Optical microscope (OM), X-Ray diffraction (XRD), Field-Emission Scanning Electron Microscopy (FE-SEM), and Energy Dispersive X-ray spectroscopy (EDX), calculating of the average particle size, and metal recovery. The results showed that the active additive used was sodium sulfate compared to sulfur. At the addition of 4.5 wt.% sodium sulfate, it was obtained phases of titanium suboxide, Ti₆O₁₁ and Ti₃O₅, with very high intensity. Recovery and grades of the reduced sample with 4.5 wt.% sodium sulfate are reached 70.91% and 94.20% Fe, respectively. Moreover, the average particle size of metallic iron increased from 11.96 µm to 38.36 µm with the addition of 4.5wt.% sodium sulfate.

1. Introduction
The primary raw materials to make TiO₂ pigment and Ti metal are ilmenite (FeTiO₃) and rutile (TiO₂). TiO₂ pigment has the best refractive index than other chemicals, and it also has good thermal stability and excellent resistance to chemical attack and ultraviolet degradation [1]. Because of these unique characteristics, TiO₂ pigment is widely applied in several industries for instance coating, papers, plastics, rubber, paints, textiles, pharmaceutical, and food [1, 2]. On the other hand, titanium metal has high chemical durability, thermal conductivity, and high strength, as a result, it is applied to thermal insulation, aerospace, marine ships, and military armor [3, 4]. High-grade titanium ores have decreased with the fast growth of the titanium processing industry. Thus, ilmenite, as an alternative raw material, must be utilized but also is complex to separate or reduce because of the impurities.

There have been some of the studies on carbothermic reduction of ilmenite with the different additives. Huang et al. [5] have reported that the particle size of the metallic iron of the sample escalated with increasing of Fe-Si to ilmenite. Also, because the silicon in this process supplies heat, the maximum temperature of the mass loss rate is reduced so that it can enhance the rapid ilmenite reduction with carbon. In another study, Liao et al. [6] examined the Fe-Si effect to improve
carbothermic reduction ilmenite placer. The addition of Fe-Si powder acts as the agent of nucleation and aggregation on reduced ilmenite.

Song et al. [7] found an addition of 2% Na$_2$B$_4$O$_7$ on carbothermic reduction of ilmenite can improve the particle size of iron up to 46.1 µm and the metallization ratio achieved 89.5%. Chen et al. [8] tested some additives such as CaF$_2$, Na$_2$SO$_4$, Na$_2$B$_4$O$_7$, NaCl, and Na$_2$CO$_3$. They reported that the metallization ratio of pre-oxidized ilmenite escalated up to 94% with the addition of 3.0% additives. Lv et al. [9] carried out the effect of sodium sulfate on pre-oxidized ilmenite reduction at a reaction temperature of 1350, 1400, and 1450 °C for 30 minutes. They reported that the metallization degree of samples would decrease during the dosage of sodium sulfate goes up to 12%, but the iron particle continuously increased with adding sodium sulfate.

In this work, ilmenite concentrate was reduced in the presence of sulfur and sodium sulfate and pulverized biomass. The addition of additive during the carbothermic reduction of ilmenite increases carbon reactivity and enlarges the size of the iron particle and titanium-rich slag [8]. This study aims to investigate the phase transformation and microstructure with sulfur and sodium sulfate as an additive. The effect of the addition dosage of additives, recovery, and the average particle size of metallic iron are discussed.

2. Material and Methods

2.1. Materials

The Indonesian ilmenite concentrate was obtained from PT. Monokem Surya, Indonesia. The mineralogical analysis and chemical composition of the ilmenite concentrates were investigated by XRD and XRF. Figure 1 showed the diffractogram of Indonesian ilmenite concentrate, which implies that the significant phases in the Indonesian ilmenite concentrates are FeTiO$_3$, TiO$_2$, and Fe$_3$O$_4$. The chemical composition of the ilmenite concentrates as measured by XRF is shown in Table 1. The Indonesian ilmenite concentrate is composed of impurities, namely Cr$_2$O$_3$, Al$_2$O$_3$, and MnO.

![Figure 1. Diffractogram of Indonesian ilmenite concentrate.](image)

| Compositions | TiO$_2$ | Fe$_2$O$_3$ | Cr$_2$O$_3$ | Al$_2$O$_3$ | MnO |
|--------------|--------|------------|-------------|-------------|-----|
| Content     | 60.27  | 35.01      | 2.11        | 1.11        | 1.50|

Table 1. Elements composition of Indonesian ilmenite concentrates (wt.%).
The reductant was the pulverized palm kernel shell biomass (particle size < 250 µm). Table 2 showed the ultimate and proximate analysis of the reductant. Sodium sulfate and sulfur were used as an additive and carboxymethyl cellulose was used as a binder.

Table 2. Elemental composition of pulverized palm kernel shell biomass.

|                      | Proximate Analysis | Ultimate Analysis |
|----------------------|--------------------|-------------------|
| Moisture in air-dried sample | 6.06               | Carbon 80.59      |
| Ash                  | 3.60               | Hydrogen 3.05     |
| Volatile Matter      | 11.12              | Nitrogen 0.79     |
| Fixed Carbon         | 79.22              | Total Sulfur 0.08 |
|                      |                    | Oxygen 11.89      |

2.2. Experimental Method

The ilmenite concentrate was homogenously mixed with pulverized biomass and additives using magnetic stirrer for 15 min. The molar ratio of C to O (in iron oxide) in the mixture was set to 1.3. The additive addition levels were set to 0%, 1.5%, 3%, and 4.5% (wt.), respectively. Next, mixtures with masses of ten-gram were mixed to homogeneity with the binder (0.5%) and distilled water (0.6%). Then, the mixture samples were compressed into a cylindrical shape (diameter: 20 mm and height: 10 mm) at a pressure of 6 ton, as shown in Figure 2. In the next step, the mixture samples were dried at 100 °C for 5 hours.

Reduction experiments were conducted in a horizontal tube electric furnace. Nitrogen was flowed into the alumina tube to release air at least for 15 min before placing the samples into the furnace until the end of reduction experiment. The samples were placed in the alumina crucible boat with samples and put into the hot zone of the furnace. The samples were reduced at temperature 1200 °C with holding time 60 min and heating rate 5 °C/min.

The reduction samples were examined by XRD with a Cu Kα source to determine phase compositions. The optical microscopy was performed to analysis the growth of the metal phase of the reduction sample. The surface morphology and chemical analysis of the reduction samples were investigated by FE-SEM with EDX. The average particle size of metallic iron was measured by the free software ImageJ using images (more than 5 pictures) from OM and FE-SEM (Backscattered electrons). The OM and Back-Scattered Electron (BSE) images with magnification 50, 100, and 1000 times of the reduced samples were used as the calculation samples. In addition, the process of determining the area of an iron particle was based on its brightness level and uses a threshold mode.

The recovery was defined as the following equation,

\[
\text{Recovery M} (\%) = \frac{c (f-t)}{f (c-t)}
\]
where $c$, $f$, and $t$ are the grade in the concentrate, the grade in the feed, and the grade in the slag, respectively. The grade in concentrated, feed, and slag was identified by EDX.

3. Result and Discussion

3.1. Phase transitions during reduction

The XRD experiments were carried out with a scanning rate from $15^\circ$ to $80^\circ$ ($2\theta$) with scan speed $2^\circ$/minute. Diffractogram of the reduction samples with different dosage of added sulfur was shown in Figure 3. The main phases of samples without additives were metallic iron, magnetite, pseudo-brookite, TiO$_2$, and FeTiO$_3$. However, several new phases appeared in the samples, such as FeO and Ti$_6$O$_{11}$. It is indicated that pulverized biomass as a reductant can reduce TiO$_2$ to titanium suboxide. At 1.5 wt.% sulfur, the intensities of FeO and Fe$_3$O$_4$ disappeared utterly, and the intensity of pseudo-brookite became strong. The XRD examination implied that a relatively high manganese content in ilmenite will react with sulfur to form manganese sulfide.

Furthermore, the diffractogram of reduction sample with dosage of 3.0 wt.% sulfur showed that the formation of Ti$_6$O$_{11}$ with high intensity followed by the formation of Ti$_3$O$_5$ with low intensity and the intensity of Fe$_3$O$_4$ disappeared utterly. The Ti$_3$O$_5$ phase became stronger when the sulfur dosage added was 4.5 wt.%. Moreover, the intensity of metallic iron significantly increased with an increasing dosage of sulfur until 3 wt.% and decreased with a dosage of 4.5 wt.% sulfur. It is due to the chemical reaction between metallic iron and sulfur to form FeS and FeS$_2$. These phases are agreed with the diffractogram of 4.5% sulfur, as shown in Figure 3.

![Diffractogram of reduction samples with different dosage of added sulfur.](image)

Figure 3. Diffractogram of reduction samples with different dosage of added sulfur.

The diffractogram of the reduction samples with different dosages of added sodium sulfate was shown in Figure 4. The sample with the addition of 1.5 wt.% sodium sulfate showed that the formation of pseudo-brookite with high intensity followed by the formation of Ti$_6$O$_{11}$ with low intensity, but the FeO phase is still formed. The magnetite phase, moreover, still formed in the sample with the addition of sodium sulfate. On the other hand, the Ti$_3$O$_5$ phase grew stronger with the addition of 4.5 wt.%
sodium sulfate compared to the addition of sulfur and TiO₂ formed with high intensity. It explains that sodium sulfate can improve the reduction ability of ilmenite. Lv et al. also reported that at temperature 1000-1100 °C CO and CO₂ will promote which are caused by the chemical reaction between sodium sulfate and carbon [9].

![Diffractogram of reduction samples with different dosages of added sodium sulfate.](image)

**Figure 4.** Diffractogram of reduction samples with different dosages of added sodium sulfate.

3.2. Morphological analysis

The growth of the metallic iron of the reduction samples enlarged gradually with increasing the additives. Figure 5 showed the optical images of reduction samples without additives and the addition of 4.5 wt.% additives. The bright area is metallic iron and a gray area is a slag containing titanium. In this image, the area of the metallic iron grew significantly with additional additives. The addition of sodium sulfate has a particle size larger than sulfur. The metallic iron in the reduction sample without additive has spherical structures, as in Figure 5a and 5d, but in the reduction sample with 4.5 wt.% additive has lump structures, as in Figure 5b, 5c, 5e, and 5f.

Figure 6 showed the effect of different additives on the average particle size of metallic iron. The average particle size of the metallic iron was markedly when addition 4.5 wt.% sodium sulfate than sulfur. The average particle size in samples without additives, 4.5 wt.% sulfur, and 4.5 wt.% sodium sulfate was 11.96 µm, 18.98 µm, and 38.36 µm, respectively. Sodium sulfate, which reacts during the process, will break down into Na₂O, Na₂S, and S. Where Na₂O will react with silica minerals to form several sodium silicates phases that have a low melting point. Besides, S will react with Fe to form FeS, which has a low melting point as well. Thus, the additive will dissolve metal particles that have an impact on the growth of metal particles. It has an impact on the evolution and aggregation of large metal particles, which are confirmed on the results of microstructure analysis [10].
Figure 5. Optical images of reduction samples. (a) and (d) micrograph of reduction sample without additive using magnification 20 and 50 times, respectively. (b) and (e) micrograph of reduction sample with 4.5% sulfur using magnification 20 and 50 times, respectively. (c) and (f) micrograph of reduction sample with 4.5% Na$_2$SO$_4$ using magnification 20 and 50 times, respectively. The bright area is metallic iron.

Figure 6. The effect of different additives on the average particle size of metallic iron.

The surface morphology and elemental mapping of the reduction samples without and with 4.5 wt.% additives are shown in Figure 7. Figure 7a showed that the metallic iron particle in the reduction sample without additives gradually grow to form spherical structures. Otherwise, in reduction samples with 4.5 wt.% additives, the metallic iron particle formed lump structures, as in Figure 7b and 7c. Besides, elemental mapping, as seen in Figure 7, showed the dispersion of metallic iron, Ti, C, S, and O. In the reduction sample with 4.5 wt.% sulfur, sulfur distributed in the metallic iron to form FeS and FeS$_2$, as in Figure 7b. It is following by the XRD results in Figure 3. On the contrary, in the reduction sample with 4.5 wt.% sodium sulfate, the distribution of sulfur was very little detected, as in Figure 7c.
Morphology and elemental mapping in the reduction samples with different additives. The additive content is 0%, 4.5% sulfur, and 4.5% Na$_2$SO$_4$ from (a) to (c), respectively. The bright area is metallic iron.

Table 3 showed the EDX analysis results of the reduction samples from Fig. 7. Conforming to the EDX result of the point marked in Figure 7 (point 1, 3, and 5), present in Table 3, it can be found that the bright area is mainly metallic iron. In Figure 7c, the reduction sample with 4.5 wt.% sodium sulfate comprises approximately 93.54% Fe, which can be classified as iron phase. Also, the gray area contains 51.86% Ti, 23.00% O, and some impurities such as Al, Si, Cr, Mn, Mg, Na, C, and S. Furthermore, the reduction sample with 4.5 wt.% sulfur, in bright area, contains 52.51% Fe and 33.05% S, it can be concluded that as iron sulfide phase. It is consistent with the XRD results, as shown in Figure 3.

| Element    | Point (wt.%) 1 | Point (wt.%) 2 | Point (wt.%) 3 | Point (wt.%) 4 | Point (wt.%) 5 | Point (wt.%) 6 |
|------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Iron (Fe)  | 92.90          | 15.77          | 52.51          | 26.09          | 93.54          | 15.95          |
| Titanium (Ti) | 3.49          | 52.08          | 5.62           | 38.50          | 2.86           | 51.86          |
| Aluminum (Al) | -             | 1.45           | 0.32           | 1.83           | 0.33           | 1.40           |
| Silicon (Si) | 0.26           | 0.33           | 0.36           | 0.68           | 0.15           | 0.46           |
| Chromium (Cr) | 0.27           | 0.08           | 0.17           | 0.36           | 0.21           | 1.05           |
| Manganese (Mn) | 0.46           | 2.46           | 0.68           | 1.28           | 0.08           | 1.70           |
| Magnesium (Mg) | 0.42           | 0.44           | 0.09           | 0.82           | 0.09           | 2.82           |
| Carbon (C)  | 0.82           | 0.74           | 2.28           | 1.57           | 1.38           | 1.14           |
| Sodium (Na) | -              | -              | -              | -              | 0.18           | 0.30           |
| Sulfur (S)  | -              | -              | 33.05          | 5.90           | 0.21           | 0.31           |
| Oxygen (O)  | 1.38           | 26.65          | 4.72           | 22.55          | 0.97           | 23.00          |

3.3. Recovery of reduction sample
The grade and recovery of Fe with different dosage of sulfur, from 0%, 1.5%, 3.0%, and 4.5% of sulfur, are shown in Figure 8a. The Fe recovery of the reduction sample with the addition of sulfur, from 0% to 4.5% of sulfur, is 72.64%, 82.65%, 69.48%, and 77.33%, respectively. Furthermore, the
Fe grade of the reduction sample with the addition of sulfur, from 0% to 4.5% of sulfur, is 76.52%, 55.15%, 90.07%, and 91.21%, respectively. Moreover, the grade and recovery of Fe with different dosages of sodium sulfate, from 0%, 1.5%, 3.0%, and 4.5% of sodium sulfate, are shown in Figure 8b. The Fe recovery of the reduction sample with the addition of sodium sulfate, from 0% to 4.5% of sodium sulfate, is 72.64%, 72.99%, 70.46%, and 70.91%, respectively. Furthermore, the Fe grade of the reduction sample with the addition of sodium sulfate, from 0% to 4.5% of sodium sulfate, is 76.52%, 90.40%, 93.58%, and 94.20%, respectively.

Figure 8. Recovery and grade of Fe with different dosages of added sulfur (a) and sodium sulfate (b).

4. Conclusion
The order of carbothermic reduction of Indonesian ilmenite can be explained as follow: first, the FeTiO$_3$, TiO$_2$, and Fe$_2$O$_3$ phase in ilmenite are reduced to Fe, FeO, Fe$_3$O$_4$, FeTi$_2$O$_5$, FeTiO$_3$, TiO$_2$, and Ti$_6$O$_{11}$. Secondly, FeTiO$_3$ and FeTi$_2$O$_5$ are reduced to Fe, TiO$_2$, Ti$_6$O$_{11}$, and Ti$_3$O$_5$. These results are beneficial to separate (e.g., magnetic separator) the iron and slag containing titanium slag. The addition of sodium sulfate can naturally improve the aggregation and growth of metallic iron particles and separate the slag and metallic iron than the addition of sulfur.

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