Effect of Briquette Thickness on Iron Nugget Formation in Fluxless Processing of Iron Sand Concentrate under Isothermal – Temperature Gradient Profiles

Zulfiadi ZULHAN,* Za’immatul HUSNAA and Eddy Agus BASUKI

Department of Metallurgical Engineering, Faculty of Mining and Petroleum Engineering, Bandung Institute of Technology, Indonesia.

(Received on August 19, 2021; accepted on November 10, 2021; J-STAGE Advance published date: January 13, 2022)

Currently, electric furnaces and blast furnaces are used to process iron sand concentrate or titanomagnetite to produce pig iron and titanium slag. The titania content in the slag ranges from 10 to 25 mass% of blast furnaces and 30 to 35 mass% of electric furnaces. The low titania content in the slag is due to the addition of flux, some iron oxide must be retained in the slag to adjust the viscosity of the slag and the mixing of iron sand concentrate with ordinary iron ore. The low titania content in the slag makes titania extraction economically unattractive. One method to achieve high titania slag is the carbothermic reduction process without flux addition. A series of experiments have been carried out on the carbothermic reduction of cylindrical briquettes consisting of iron sand concentrate and coal under an isothermal – temperature gradient profile up to 1380°C to produce iron nuggets separated from slag. The briquettes have a diameter of 13 mm, and the thickness varied from 2 to 18 mm. The results showed that the thickness of the briquettes significantly affected the iron recovery in the nuggets. The briquettes with 2 mm thickness showed higher iron recovery in the nugget. The study also found that the sulfur content in coal may have contributed to the formation of iron nuggets.

KEY WORDS: iron sand; titanomagnetite; iron nugget; fluxless; carbothermic.

1. Introduction

Iron sand concentrate (ISC) from the beach or titanomagnetite (TTM) in general have not been widely used as a raw material for iron and steel production. Until now, New Zealand Steel is the only iron and steel plant in the world that uses ISC as a raw material where the prereduction takes place in multi hearth furnaces and rotary kilns followed by further reduction and smelting in electric furnaces.1) Similar plants are operated by Evraz Highveld Steel & Vanadium, South Africa, using titanomagnetite from ore deposits.2) The main product from both plants is pig iron which is further processed into steel and the by-products are vanadium slag and rotary kilns followed by further reduction and smelting in electric furnaces.3) The main product from both plants is pig iron which is further processed into steel and the by-products are vanadium slag and titanite slag with TiO$_2$ content about 30–35 mass%. Another technology is blast furnace, which is applied in Panzhihua,4) Chengde,5) and NTMK.6) The products are similar to an electric furnace with the difference in TiO$_2$ content in slag of about 10–25 mass% depending on the amount flux addition, the chemical composition of raw material and the proportion of TTM in the mixture with ordinary iron ore. Due to the low TiO$_2$ content in the slag from electric furnaces or blast furnaces, other techniques have to be developed.

Reduction of titanomagnetite by hydrogen gas,6–8) carbon monoxide gas9–12) and the combination of carbon monoxide gas and hydrogen gas13) at temperature ≤ 1200°C have been widely reported. Titanomagnetite was suggested to be preoxidized with the aim of converting titanomagnetite or magnetite to hematite to facilitate the reduction of iron-bearing oxides to metallic iron.8,10,11,13) Solid-state reduction of titanomagnetite by graphite,14–16) coal,17,18) and coke20) in the temperature range of 1000–1350°C was also investigated. In general, the iron-bearing oxides in titanomagnetite were reduced to metallic iron at a temperature higher than 900°C and the degree of metallization can be enhanced by increasing the reduction temperature. However, the above-mentioned reduction requires a smelting step to separate the metallic iron from the other oxides.

The combination of solid-state reduction with magnetic separator was reported by Geng et al.21) and Zhao et al.22) in which experiments were carried out by embedding ISC pellet in bituminous coal at a temperature range...
100–1400°C. They suggested that the optimum temperature was 1200°C and reduction time was 2–2.5 h. The addition of sodium sulfate up to 15 mass% into the ISC was also proposed by Geng et al.23 and Gao et al.24 with the aim of reducing the melting point of iron by forming troilite (FeS) which promotes iron migration, accumulation, and growth into larger particle at 1200–1250°C for 1–5 h. However, the presence of sulfur is undesirable in iron product. To overcome the pick-up of sulphur in the iron product, Zhang et al. overcame the pick-up of sulphur in the iron product. To overcome the pick-up of sulphur in the iron product, Zhang et al.25 introduced the addition of sodium carbonate into TTM up to 100 mass% and the formation of iron nugget was reduced. The optimum conditions were the addition of 70 mass% sodium carbonate, the molar ratio of C from coal to Fe in TTM was 1.70, the reduction temperature of 1200°C and reduction time of 2 h. Recently, Zhao et al.26 added fluorite to increase the degree of metallization and iron recovery at a reduction temperature of 1200°C and a reduction time of 1 h.

The formation of iron nuggets without additives was reported by Hu et al.27 by mixing TTM with coal and reduced under the combination of unisothermal from room temperature at a heating rate of 5°C/min and isothermal for 30 min at 900, 1000, 1200, and 1300°C with a total treatment time of 440 min. Similar results were reported by our previous work in which iron nuggets were formed on the surface of reduced composite pellets by the carbothermic reduction of ISC under an isothermal-temperature gradient profile starting from isothermal at 1200°C and increasing to a final temperature of 1380°C at a heating rate of 6.33°C/min with a total reduction time of less than 150 min.28 To improve iron recovery in the nugget without additives, in this paper we report the effect of briquette thickness.

2. Experimental

Iron sand concentrate (ISC) from West Java, Indonesia, was dried in an oven for 24 h at 135°C. The grain size of ISC was less than 0.212 mm (−65#) and the detail of grain size distribution is given in Table 1. The chemical composition was determined by X-ray fluorescence (XRF) as listed in Table 2 wherein the iron content was 55.35 mass% and titanium 6.70 mass%. The X-ray diffraction (XRD) pattern in Fig. 1 shows that the main minerals in the ISC were titanomagnetite (Fe2.75Ti0.25O4) and magnetite (Fe3O4) with small amount of ilmenite (FeTiO3). The results are similar to those reported by other researchers who used Indonesian ISC as experimental material.15,24,27) The simultaneous presence of more than one mineral at the same peak in the XRD pattern in Fig. 1 was also reported by Hu et al.28)

Table 1. Grain size distribution of iron sand concentrate (mass%).

<table>
<thead>
<tr>
<th>Size Distribution (mm)</th>
<th>Mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>~325# (~0.044 mm)</td>
<td>1.62</td>
</tr>
<tr>
<td>~80#+325# (0.044–0.177 mm)</td>
<td>70.1</td>
</tr>
<tr>
<td>~80# (~0.177 mm)</td>
<td>21.50</td>
</tr>
</tbody>
</table>

Table 2. Chemical composition of iron sand concentrate (mass%).

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Ti</th>
<th>Al</th>
<th>Mg</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass%</td>
<td>55.35</td>
<td>6.70</td>
<td>1.88</td>
<td>1.12</td>
<td>1.32</td>
<td>0.39</td>
<td>0.033</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Reducing agent was prepared using a roll crusher, and a ball mill to obtain a grain size of less than 35# (~0.425 mm). The coal was dried in an oven for 24 h at 105°C to remove its moisture content. The proximate and ultimate analyses of coal are listed in Tables 3 and 4.

The ISC was mixed with 30 mass% coal where the weight of ISC was used as the basis. The mixture was formed into cylindrical briquettes using a 13 mm diameter die with the help of a hydraulic press. The amount of mixture was adjusted so that the thickness of the briquettes was about 2 mm, 6 mm, 9 mm, 14 mm, and 18 mm, respectively, as shown in Fig. 2. The weight of the briquettes was in the range of 1.17 g for 2 mm briquette thickness to 8.07 g for 18 mm briquette thickness.

Before a briquette was loaded into a 20-mL alumina crucible equipped with a lid, a layer of coal was prepared at the bottom of the crucible. After the briquette was loaded in the crucible, more coal was added in the crucible to maintain the reducing environment and support the reduction by covering the entire surface of the briquette. The total addition of coal for this purpose was 3 g for briquettes with a thickness of 2 mm to 11 g for briquettes with a thickness of 18 mm. Finally, 1 g of alumina powder was added at the top to minimize the penetration of oxygen from the atmosphere during the reduction process. The addition of coal was a combination of self-reducing briquette and briquette embedded in coal. The experiments were carried out in a muffle furnace without controlling the atmosphere and under the isothermal-temperature gradient profile.29) Three briquettes were prepared and reduced for each experimental parameter to obtain reliable results. After the experiment, the crucibles were removed from the muffle furnace, and reduced briquettes were cooled to room temperature in the crucible. The reduced briquettes were weighed, documented, and...
then examined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). After the reduced briquette was crushed using a mortar manually, the iron nuggets were separated from the slag by hand sorting. The nuggets and slag were weighed, and the size of the nuggets was measured by a caliper.

3. Results and Discussion

3.1. Temperature Pattern and Mechanism of Nugget Formation

Based on our previous work, reduction of ISC/coal composite pellets with a diameter of 15.5–16.5 mm under an isothermal-temperature gradient profiles produced iron nuggets which were separated from other oxides. Iron recovery in iron nuggets was in the range of 58–66%. To increase iron recovery in nuggets, the effect of pellet diameter should be investigated. Since pellets of different diameters were difficult to produce consistently using a rotating disk, it was decided to prepare a mixture of ISC with coal in the form of briquettes.

Two temperature patterns were used to evaluate the effect of briquette thickness on the formation of iron nuggets as shown in Fig. 3. Initial temperature and heating rate varied in those temperature pattern. The furnace temperature was set at 800°C as initial temperature for pattern A. After the crucible was inserted into the furnace, the furnace temperature was held for 20 min at 800°C and then the furnace temperature was increased to 1380°C with a heating rate of 6.67°C/min. The holding time at final temperature for pattern A was 40 min. In pattern B, the initial temperature of 1100°C was held for 20 min then the temperature was increased to 1380°C with a heating rate of 4.67°C/min. The holding time at the final temperature of 1380°C for pattern B was 40 min.

The formation of iron nuggets was studied in more detail using pattern A as shown in Figs. 3(a)–3(e) for 2 mm thickness briquettes. After a reduction time of 20 min at 800°C (point 1 in Fig. 3), the crucible was removed from the furnace. The results showed that the reduced briquettes were weak, easily crushed and did not form nuggets (Fig. 3(a)). As investigated previously, at 800°C the magnetite in the ISC was reduced to wustite and no metallic iron was formed. A similar appearance to Fig. 3(a) was observed on the reduced briquette after a reduction time of 65 min (Point 2 in Fig. 3) as shown in Fig. 3(b). Previous studies have shown that at 1100°C titanomagnetite was transformed and reduced to ilmenite and metallic iron (Fig. 3(c)).

Therefore, the surface of reduced briquette at 1100°C after a reduction time of 65 min (Fig. 3(b)) was the examined by SEM - BSE (scanning electron microscope - backscattered electrons) as shown in Fig. 4(a) for 500× magnification. Metallic iron (light gray in Fig. 4(a)) formed on the surface of the reduced briquette and some metallic iron grew like whiskers. From Fig. 4(b) with a magnification of 3,000× (Area A in Fig. 4(a)), it was clearly seen that metallic iron nucleated and formed globular shapes with a size about 1 μm and less. The length of the whiskers was about 6 μm.

When the temperature reached 1380°C (point 3 in Fig. 3), small nuggets were clearly visible on the surface of reduced briquette as shown in Fig. 3(c). The BSE image in Fig. 4(c) shows the iron nuggets with the diameter of about 1 mm. The iron nuggets were formed due to the migration of small particles of metallic iron in the form of globular or whisker, interconnected from one particle to another, aggregated and agglomerated to form larger globular (nugget) during an increase in temperature from 1100–1380°C with a heating rate of 6.67°C/min. Reduction of iron oxide occurred also during heating. Figure 4(d) shows many small globular particles of metallic iron with a size of less than 1 μm.

As the holding time increased at 1380°C for 20 min, the size of the nuggets became larger as shown in Fig. 3(d). The BSE image is shown in Figs. 4(e) and 4(f). The agglomeration of small particles into larger globular particles leaved cavities and pores within the reduced briquette as shown in Fig. 4(f) which provided pathways for the reduction
gas from the embedded coal to react with the iron-bearing oxides in the center of the briquette. As the holding time increased longer at 1380°C to 40 min, larger iron nuggets revealed on the surface of reduced briquette which are clearly visible in Fig. 3(e). The number of iron nuggets in Fig. 3(e) was less than those in Fig. 3(d) due to the combination and agglomeration of small nuggets into larger nuggets.

From Figs. 3(c) to 3(e) it was obviously that the iron nugget tended to form on the surface of the briquettes which can be caused by:

1. the interaction of metallic iron on the surface of the briquettes with the embedded coal so that the carbon from coal dissolved in the metallic iron (carburization) which lowered the liquidus temperature of iron nugget, and
2. the migration of metallic iron from the center or inside of the briquette to the outside to the surface of briquette due to higher temperature on surface which led to the formation of larger particles on the surface through the aggregation and agglomeration of smaller particles.

Hu et al. reported that the carbon content in the iron
A nugget formed from the reduction of TTM briquettes by coal was 1.39 and 1.51 mass% at 1300 and 1350°C, respectively. At higher temperatures, the carbon content in iron nuggets might increase which had an impact on lowering metal liquidus temperature.

3.2. Iron Nugget Size and Iron Recovery

Comparison of iron nuggets formed on the surface of reduced briquettes for different thicknesses of briquettes using temperature patterns A and B is shown in Fig. 5. Briefly, there was no difference between pattern A and pattern B for the formation, size, and shape of the nuggets. As the thickness of the briquettes increased, the number of nuggets on the reduced briquettes also increased. Slag and iron nuggets separated manually by hand sorting from the slag are shown in Fig. 6 for the briquette thicknesses of 2 mm, 9 mm, and 18 mm. It was clear that the number of iron nuggets increased with increasing briquette thickness.

The number of iron nuggets produced from various thicknesses of briquettes is shown in Fig. 7(a). The temperature patterns A and B showed similar trend where the amount of iron nugget produced from the briquette thickness of 2 mm increased and reached its maximum value at 9 mm briquette thickness. After that, the number of nuggets decreased slightly. Figure 7(b) shows the size of the iron nugget for temperature patterns A and B taken from the average value of the three reduced briquettes for each experimental parameter. The trends were similar for temperature patterns A and B where the average size was between 1–2 mm. The detailed size distribution is shown in Figs. 7(c) and 7(d) for temperature patterns A and B, respectively, where the highest number of particles had a size between 1–2 mm, followed by sizes 0.3–1 mm, 2–3 mm, 3–4 mm and 4–5 mm. In general, the temperature patterns A and B resulted in a similar size distribution. The size of iron nugget that can be separated manually was larger than 0.35 mm. The size of iron nugget that was less than 0.35 mm remained in the slag.

The initial briquette weight, iron nugget weight and slag weight from temperature patterns A and B can be seen in Fig. 8(a). The weight of the iron nuggets higher or equal to

<table>
<thead>
<tr>
<th>Briquette thicknesses</th>
<th>Temperature pattern A</th>
<th>Temperature pattern B</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 mm</td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>6 mm</td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>9 mm</td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>14 mm</td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>18 mm</td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
</tr>
</tbody>
</table>

Fig. 5. Iron nuggets on the surface of reduced briquettes for different thicknesses of briquettes and temperature patterns. (Online version in color.)

(a) Nuggets from briquette 2 mm thick.  
(b) Slag from briquette 2 mm thick.  
(c) Nuggets from briquette 9 mm thick.  
(d) Slag from briquette 9 mm thick.  
(e) Nuggets from briquette 18 mm thick.  
(f) Slag from briquette 18 mm thick.

Fig. 6. Iron nuggets and slag produced from temperature pattern A. (Online version in color.)
the weight of the slag was observed in the briquettes with a thickness of 2 mm. In briquettes with other thicknesses, weight of slag was higher than weight of iron nugget which indicated that the amount of iron nuggets was less. To analyze the data more accurately, the iron recovery was calculated using the following equation:

\[
\text{Iron recovery in nuggets (\%)} = \frac{W_N}{W_{Fe}} \times 100\% \quad (1)
\]

where \(W_N\) is the weight of iron nuggets from the reduced briquettes and \(W_{Fe}\) is weight of iron in the initial briquettes.

The relationship between initial briquette thickness and iron recovery in the nuggets is shown in Fig. 8(b). The
highest iron recovery was achieved from the initial briquette thickness of 2 mm. The thicker the briquettes, the iron recovery tends to decrease. This phenomenon can be explained by observing the location of nugget formation. From Fig. 5 it can be seen that nuggets were formed on the surface of the reduced briquettes. By using thinner briquettes, the distance between the center of the briquette to the surface was shorter, so the metallic iron that was reduced in the center of the briquette had the ability to move faster to the surface. Heat from the surrounding crucible coming from the muffle furnace or from outside of briquette can reach the inside of the briquette more quickly for thinner briquettes during a gradient temperature stage with a certain heating rate. In general, the temperature pattern A resulted in higher iron recovery compared to the temperature pattern B. The main difference the pattern A and B was the initial temperature and the heating rate that affected the iron recovery. The higher initial temperature caused the formation of a liquid metal phase on the surface of the briquette which inhibited the diffusion of the reduction gas from the embedded coal to the center of the briquette. Oxides containing iron will be reduced first on the surface of the briquettes rather than the inside of the briquettes.

As previously mentioned, nugget sizes larger than 0.35 mm can be separated manually and counted as metal for iron recovery calculations. Nugget smaller than 0.35 mm remained in the slag. To improve iron recovery, smaller iron nuggets can be recovered by applications such as magnetic separators. For industrial practice, the production of small and thin agglomerates can be achieved using a pelletizing machine to produce micro pellets.

3.3. Optical Microscopy and SEM Analysis of Iron Nuggets

The bisections of the iron nuggets were prepared for optical microscopy observation and analysis by SEM-EDS. The results of observing the microstructure using an optical microscope are shown in Fig. 9 from three different initial thicknesses of briquettes and from two temperature patterns. It is clearly seen that the two temperature patterns resulted in a relatively similar iron nugget microstructure. The grain size was found larger in iron nuggets produced from the 2 mm thickness of the briquettes. Dendritic structure and smaller grain size were observed in the nuggets produced from thicker briquettes. Pores were also observed in all iron nuggets caused by the process of agglomeration of small particles into larger sized nuggets that did not take place completely because the particles were in semi molten phase.

The microstructure of the nugget produced from the 2 mm thick briquette (area B in Fig. 9(a)) was further examined by SEM-EDS, as shown in Fig. 10(a), while the EDS mapping results are depicted in Figs. 10(b) to 10(e). This finding indicated that the iron content was generally well distributed in the bisection of iron nugget, as seen in Fig. 10(b), except at the grain boundary areas where the iron content decreased in several locations. The depletion of iron at these areas was caused by the presence of sulfur, as shown in Fig. 10(c), where the sulfur in iron nuggets tended to segregate at the grain boundaries. It is believed that most of sulfur came from coal because the sulfur content in the ISC was negligible. The combination of sulfur with iron formed troilite (FeS) that has a lower melting point. The presence of this troilite particles can be used as the site for nucleation and initiation of iron nugget formation, in addition to carburization as previously described. The effect of sodium sulfate on ISC reduction with troilite formation resulting larger particles at 1 200–1 250°C has been reported by Geng et al.23) and Gao et al.24) It was also found, as indicated in Fig. 10(d), that silicon was formed from silica reduction in ISC and coal with carbon contained in the iron nuggets. In contrast to sulfur which tended to accumulate at the grain boundaries, carbon was distributed throughout the grain although unevenly due to solidification process as shown in Fig. 10(e).

![Fig. 9. Microstructures of nuggets produced from different thicknesses of briquettes and different temperature patterns. (Online version in color.)](image-url)
The detailed chemical composition of the iron nugget in area C of Fig. 10(a) is shown in Fig. 11. Area C was selected to obtain detail observation of the area where sulfur and silicon are coexisted. In the iron matrix (point D in Fig. 11), the vanadium was found in the nugget, while the initial chemical analysis by XRF given in Table 1 shows that vanadium is negligible. This negligible levels of vanadium in the ISC have also been reported by other researchers who used ISC from Indonesia as an experimental material in their studies.\textsuperscript{15,21–24,27} The present of vanadium as detected by EDS in iron nuggets could be due to uneven preparation of the ISC samples which in certain areas had relatively high levels of vanadium. This also confirmed by the absence of vanadium at points E, G and I in Fig. 11 which shows a
similar chemical composition.

Point F in Fig. 11 shows a silicon content of 80.4 mass% along with 9.9 mass% titanium with small amounts of carbon and oxygen. This indicated that silicon and titanium might present as an oxide trapped between one metallic iron particle and another during agglomeration in the process of larger nugget formation. Meanwhile, point H in Fig. 11 might present as an oxide trapped between one metallic iron bond and oxygen. This indicated that silicon and titanium along with 9.9 mass% titanium with small amounts of carbon and oxygen. This combination of sulfur and iron at this composition represented FeS compounds and gives advantage to provide nucleation sites for the initiation of nuggets formation. However, the presence of sulfur in the iron product is essentially not expected because this requires efforts and costs to remove it.

4. Conclusion

The effect of briquette thicknesses on the iron recovery in the nuggets was investigated using two different temperature patterns which were a combination of isothermal and temperature gradient. The results showed that iron recovery in nuggets can be increased by using thinner briquettes. By using the briquettes 2 mm thick with a diameter of 13 mm produced by mixing iron sand concentrate with 30 mass% coal, iron recovery of 77% can be achieved by manually selecting nuggets by hand sorting for sizes larger than 0.35 mm from the reduced briquettes. The iron recovery can be further improved by using for example magnetic separation techniques to recover nuggets less than 0.35 mm in size. The study also found that the sulfur content in coal may have contributed to the formation of nuggets.

Acknowledgement

The authors would like to thank the Ministry of Research, Technology, and Higher Education of the Republic of Indonesia for funding this research and PT. Sumber Baja Prima, Indonesia, for providing the iron sand concentrate.

REFERENCES


10) E. Park and O. Ostrovski: ISIJ Int., 44 (2004), 74. https://doi.org/10.2355/isijinternational.44.74


