REDUCTION BEHAVIOR OF ASSMANG AND COMILOG ORE IN THE SiMn PROCESS

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Abstract

The reduction behavior of raw materials from Assmang and Comilog based charges were experimentally investigated with CO gas up to 1600 °C. Quartz, HC FeMn slag or limestone were added to Assmang or Comilog according to the SiMn production charge, and mass loss results were obtained by using a TGA furnace. The results showed that particle size, type of manganese ore and mixture have close relationship to the reduction behavior of raw materials during MnO and SiO_2 reduction. The influence of particle size to mass loss was apparent when Assmang or Comilog was mixed with only coke (FeMn) while it became insignificant when quartz and HC FeMn slag (SiMn) were added. This implied that quartz and HC FeMn slag had favored the incipient slag formation regardless of particle size. This explained the similar mass loss tendencies of SiMn charge samples between 1200-1500 °C, contrary to FeMn charge samples where different particle sizes showed significant difference in mass loss. Also, while FeMn charge samples showed progressive mass loss, SiMn charge samples showed diminutive mass loss until 1500 °C. However, rapid mass losses were observed with SiMn charge samples in this study above 1500 °C, and they have occurred at different temperatures. This implied rapid reduction of MnO and SiO_2 and the type of ore and addition of HC FeMn slag have significant influence determining these temperatures. The temperatures observed for the rapid mass loss were approximately 1503 °C (Quartz and HC FeMn slag addition in Assmang), 1543 °C (Quartz addition in Assmang) and 1580-1587 °C (Quartz and limestone addition in Comilog), respectively. These temperatures also showed indications of possible SiMn production at process temperatures lower than 1550 °C.

Introduction

Manganese ferroalloys, such as ferromanganese (FeMn) and silicomanganese (SiMn), are commonly consumed in steel industries as additives to achieve various grades of steels with high quality [1, 4]. As an alloying unit, the addition of FeMn or SiMn will influence the strength, toughness and hardness of steel products. They also serve as excellent desulfurizers and deoxidizers to prevent brittle and porous steel products [1-11].

The more use of SiMn as additives in steel industries is expected to advance at a faster rate than FeMn consumption [1, 2, 12]. As deoxidizers, SiMn is more effective than FeMn. Deoxidation of steel with SiMn have given cleaner results than individual addition of ferrosilicon (FeSi) and FeMn [2]. Also, the use of SiMn is more advantageous because it contains less carbon, phosphorus, sulphur, aluminium and nitrogen compared to a mixture of FeMn and FeSi

[2]. These features of SiMn addition in steel industries makes the production of high quality SiMn an important task. However, the choice of using FeMn or SiMn in the end will always be a question of cost, and thus dependent on the global market.

Considering the process reactions for SiMn, a temperature of 1600-1650 °C is necessary to obtain SiMn with sufficiently high content of silicon and discard slag with low MnO. At this temperature, the final reduction of MnO and SiO_2 can take place as shown in the following reactions:

$$MnO_{(l)} + C = Mn_{(l)} + CO_{(g)} \qquad (1)$$
$$SiO_{2(l)} + 2C = Si_{(l)} + 2CO_{(g)} \qquad (2)$$

Also, the reduction of MnO and SiO_2 are considered to occur simultaneously in the SiMn process. Thus, the slag/metal exchange reaction of Mn and Si, which is the combination of reactions 1 and 2, has to be taken into account:

$$SiO_{2(l)} + 2Mn_{(l)} = Si_{(1)} + 2MnO_{(l)} \qquad (3)$$
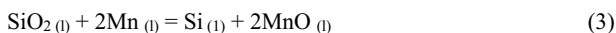
Current studies showing excavation of industrial and pilot scale furnaces provide information that reduction of MnO and SiO_2 occurs mainly at the top part of the coke bed [13, 14]. This implies that most of the raw materials are priory melted into a slag phase, and the reduction of MnO and SiO_2 occurs on the top part of the coke bed where the slag is in contact with carbon reductants. Thus, different charge materials are likely to exhibit different reduction behavior during the process because of their different melting properties such as temperature. Various types of manganese ores and high-carbon ferromanganese (HC FeMn) slag have been previously reported to have different "melting temperatures" [14, 15]. The "melting temperature" was considered as the temperature when the ore starts to form liquid slag and behaves as a liquid. Assmang, Gabonese, CVRD ore, CVRD sinter and HC FeMn slag were measured by a sessile drop furnace experiment, which gave the "melting temperatures" of approximately 1446, 1485, 1461, 1395 and 1220 °C, respectively. These different temperatures are assumed to give significant influence during the SiMn process.

While the process mechanism of FeMn have been extensively studied during the last 20 years, less effort was use to ascertain the process mechanism of SiMn. Although the process reactions of SiMn has previously been studied [2,16], only few studies considering the reduction behavior between raw materials have been reported. Therefore, the present study focuses on an experimental investigation of the reduction behavior of raw materials in the SiMn process. In this case, two different manganese ores, Assmang and Comilog, were used to compare the reduction behavior during the SiMn process. Quartz, HC FeMn slag or limestone were added into Assmang or Comilog according to a SiMn charge, and the reduction behavior of each different charge sample was observed.

Experimental

The objective of this study was to conduct an experimental investigation to ascertain the reduction behavior of raw materials in the SiMn process. The characterization and preparation of raw materials, the TGA furnace and the experimental conditions are described in the next subsections.

A. Raw Materials and TGA Furnace

Assmang and Comilog ores were used as the main manganese source in this experiment. The chemical compositions of Assmang, Comilog, coke, quartz, HC FeMn slag and limestone used in this experiment are shown in Table I.

Table 1. Chemical Composition of Raw Materials for SiMn Process [dry mass %]

Raw Materials	MnO	MnO₂	SiO₂	Fe₂O₃	CaO	MgO	Al₂O₃	CO₂	C	Total
Assmang	32.69	33.22	5.77	15.06	6.26	1.10	0.26	3.52	0.27	98.15
Comilog	3.91	69.40	6.50	6.47	0.29	0.13	6.90	0.10	-	93.70
Coke	0.04	-	5.60	0.86	0.42	0.22	2.79	-	87.68	97.61
Quartz	0.14	-	93.85	-	0.09	0.05	1.19	-	-	95.32
HC FeMn Slag	35.23	-	25.45	-	18.45	7.53	12.30	-	0.40	99.36
Limestone	-	-	0.96	-	51.98	0.96	0.26	45.72	-	99.88

Considering the amount of oxides (CaO, MgO and Al₂O₃) for the two types of ore, Assmang contained a relatively high amount of CaO (6.34 mass %) and was considered as a basic ore. On the other hand, Comilog contained a relatively high amount of Al₂O₃ (6.70 mass %) and was considered as an acidic ore. Basic ores are known to have a relatively high melting temperature compared to acidic ores, which are considered to have a lower melting temperature [13-15]. Polish coke was used as the carbon reductant. Each of the raw material was prepared in two different size groups, 0.6-1.6 and 4.0-6.3 mm, to observe the influence of particle size during the reduction process.

The schematic of the TGA furnace is shown in Figure 1. The furnace can endure temperatures up to 1700 °C and the maximum heating rate is up to 25 °C/min. A mass balance is installed at the top and a Molybdenum (Mo)-wire was used to suspend the crucible inside the furnace. Graphite crucibles (36 mm outer diameter, 30 mm inner diameter, 70 mm height and 61 mm deep) were used to contain each charge sample in this experiment.
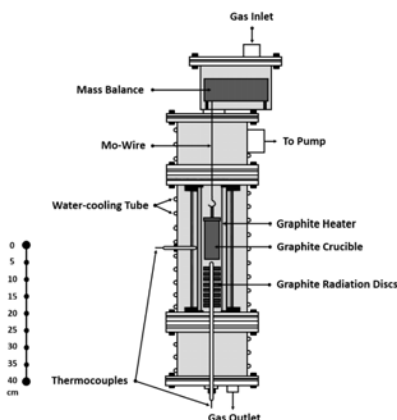

Figure 1. Experimental setup: schematic of thermo-weight furnace.

B. Procedure

Profiles for each charge sample were prepared according to Table II. Raw materials for each charge were measured and mixed into a graphite crucible. Then the graphite crucible was suspended by hooking it to the Mo-wire inside the furnace chamber.

Table II. Profile for Each Charge Sample [g]

Charge No.	Size [mm]	Assmang	Comilog	Coke	Quartz	HC FeMn Slag	Limestone	Total
As. 1A	0.6-1.6	23	-	7	-	-	-	30
As. 1B	4.0-6.3							
As. 2A	0.6-1.6	23	-	7	10	-	-	40
As. 2B	4.0-6.3							
As. 3A	0.6-1.6	13	-	7	7	13	-	40
As. 3B	4.0-6.3							
Com. 1A	0.6-1.6	-	23	7	-	-	-	30
Com. 1B	4.0-6.3							
Com. 2A	0.6-1.6	-	23	7	6	-	-	36
Com. 2B	4.0-6.3							
Com. 3A	0.6-1.6	-	18	6	7	-	5	36
Com. 3B	4.0-6.3							

The furnace was then sealed and the chamber was initially cleaned with pure Ar gas (99.9999 %). Next, heat was applied to the furnace according to temperature profile in Figure 2.
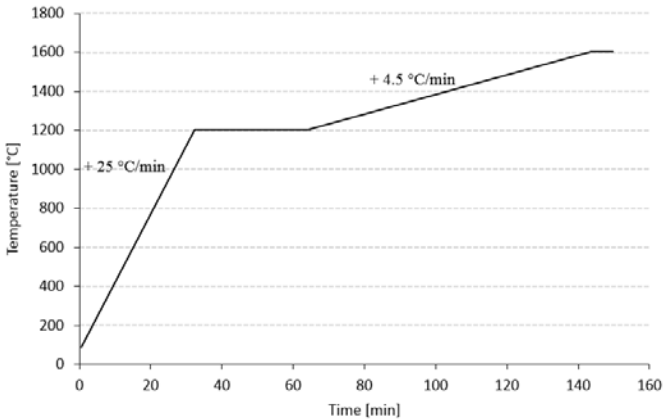

Figure 2. Temperature profile.

Initially, the furnace was heated up to 1200 °C (+ 25 °C/min): 0.5 l/min of Ar gas was supplied until the crucible temperature was approximately 500 °C and the Ar gas was converted to 0.5 l/min of CO gas above 500 °C. Each charge sample was held for 30 minutes at 1200 °C and it was assumed complete pre-reduction during this step [2, 13]. Then, further heating was done until 1600 °C (+ 4.5 °C/min). Finally, each charge sample was held for 5 minutes at 1600 °C and cooled down to room temperature. During the cooling, CO gas was supplied until the crucible temperature dropped down to approximately 500 °C and was converted to Ar gas until complete cooling. The weight loss (% mass loss) of each charge sample was recorded and data

were logged every 5 seconds during the experiment. Lastly, each charge sample was prepared by mounting in epoxy to be further analyzed. The JEOL JXA-8500, an EPMA (Electron Probe Micro-Analysis) type, was used to analyze slag compositions.

Results and Discussion

The results from the TGA furnace and EPMA analysis are presented in this section. Mass loss with time of each charge sample is described between 1200 and 1600 °C. The comparison of all charge samples is shown to see the difference of reduction behavior regarding particles size, type of manganese ore and mixture. Also, the comparison of the primary slag (calculated) and final slag (measured) of each charge samples is discussed.

The mass loss and reduction behavior of each charge sample during the reduction of MnO and SiO_2 at different temperatures between 1200 to 1600 °C is described in Figure 3. The results showed that the reduction behavior during the MnO and SiO_2 reduction are differed using different particle size, type of manganese ore and mixture.
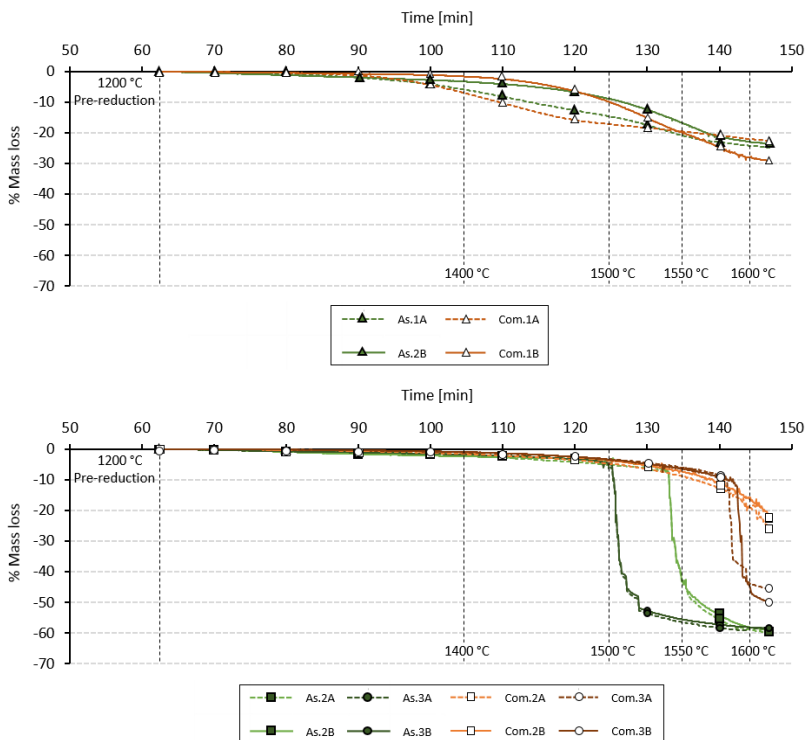
Figure 3. MnO and SiO_2 reduction results of FeMn charge samples (top) and SiMn charge samples (bottom) described in percent mass loss with time.

The influence of particle sizes showed different results for FeMn and SiMn charge samples. The mass loss difference between particle sizes was mainly observed with Assmang or Comilog mixed with only coke (As.1 and Com.1) which were representatives of FeMn charge samples. FeMn charge samples with particle sizes between 0.6-1.6 mm showed more mass loss than with particles sizes between 4.0-6.3 mm. However, when Assmang or Comilog was mixed with quartz and HC FeMn slag, which were representatives of SiMn charge samples, the mass loss difference between two different size groups were insignificant compared to FeMn charge samples during the reduction. This comparison between FeMn and SiMn charge samples shows indication that particle size might not be an evaluating variable during the reduction of MnO and SiO_2 for SiMn process. If manganese ore and quartz particles are completely dissolved into a slag phase shortly after pre-reduction, particle size will no longer be a variable influencing the mass loss and further the reduction of MnO and SiO_2. While solid MnO is present until the liquidus temperature in the FeMn process [2, 17], considerable amount of molten slag phase seems to generate during the early stages in SiMn charges.

The type of manganese ore and mixture also showed different reduction behavior during the experiment condition. For SiMn charge samples, the percent mass losses from 1200 to 1500 °C were relatively low, which were between 0 to 5 %, and similar regardless of particle size, type of manganese ore and mixture. The similar mass losses can be explained by the dominating incipient slag phase, which is generated at early process temperature for SiMn charges. Besides coke, all particles are melted into a slag phase. However, the low mass loss of SiMn charges until elevated temperatures (before rapid mass loss) indicates insignificant reduction of MnO and SiO_2. The slag composition for primary (calculated) and after 1600 °C, (measured) is shown in Table III, and the comparison of a_{MnO} shows why the MnO reduction is not occurring until a higher temperature is reached. Note that all iron oxides are assumed to be completely reduced during pre-reduction and the main slag components are MnO, SiO_2, CaO, MgO and Al_2O_3 in all charge samples.

Table III. Comparison of Primary and Final Slag Composition [mass %], and calculated activities of MnO and SiO2 by using FACTsage

Charge No.	Primary Slag Composition (Calculated): 1200 °C							
	MnO	SiO₂	CaO	MgO	Al₂O₃	Total	a_MnO	a_SiO₂
As. 1	81.70	7.88	8.55	1.50	0.36	99.99	0.810	0.002
As. 2	51.40	41.55	5.41	0.96	0.69	100.01	0.095	0.448
As. 3	42.17	37.30	10.90	3.80	5.81	99.98	0.128	0.168
Com. 1	81.45	8.72	0.39	0.18	9.27	100.01	0.655	0.004
Com. 2	61.33	30.92	0.31	0.15	7.29	100.00	0.215	0.152
Com. 3	48.52	34.11	11.1	0.32	5.94	99.99	0.166	0.140
Charge No.	Final Slag Composition (Measured by EPMA): 1600 °C							
	MnO	SiO₂	CaO	MgO	Al₂O₃	Total	a_MnO	a_SiO₂
As. 1A	16.27	40.55	35.79	5.93	1.46	100.00	0.103	0.080
As. 1B	20.77	40.47	33.71	3.69	1.36	100.00	0.112	0.093
As. 2A	- Not observed -							
As. 2B	3.91	57.15	30.53	4.51	3.89	99.99	0.002	0.646
As. 3A	9.59	49.35	23.67	5.49	11.89	99.99	0.011	0.344
As. 3B	6.80	48.83	25.95	6.29	12.13	100.00	0.009	0.300
Com. 1A	- Not available -							
Com. 1B	11.22	10.36	3.68	0.20	64.75	95.18	0.049	0.006
Com. 2A	- Not available -							
Com. 2B	12.30	43.20	2.60	0.01	33.00	95.30	0.008	0.412
Com. 3A	- Not available -							
Com. 3B	3.80	40.30	38.00	0.40	13.8	96.40	0.014	0.127

The change of a_{MnO} from 1200 to 1600 °C for FeMn and SiMn charges shows good accordance with the mass losses between 1200 to 1500 °C. The difference of a_{MnO} of FeMn charges, As.1 and Com.1, from 1200 and 1600 °C is relatively significant compared to SiMn charges. This indicates the entity of the driving force for MnO reduction is in existence, and the progressive mass loss of As.1 and Com.1 shows good accordance. The low activity of MnO in SiMn charges also explain the insignificant reduction of MnO at lower temperatures.

The rapid mass losses, which were also observed with SiMn charges above 1500 °C, showed close relationship with the type of manganese ore and mixture. The starting temperature of the rapid mass loss of As.2 and As.3 was approximately 1543 and 1503 °C, and had a_{MnO} of 0.095 and 0.128, respectively. As.3 will thus have a higher driving force which explains the lower reduction temperature. The similar rapid mass loss was also observed with Comilog but only with Com.3 and at higher temperature of 1580-1587 °C. Com.2 and Com.3 has a_{MnO} of 0.215 and 0.116. Hence, the difference in reduction temperature cannot be explained by the driving force, as Com.2 has a higher driving force. The palpable reduction behavior SiMn charges is that rapid reduction of MnO and SiO_2 occurs at lower temperature with Assmang than Comilog. The amount of iron oxides in the ore can give some implication considering the different reduction behavior in SiMn charges. As Assmang has a higher iron content than Comilog, the amount of initial iron after pre-reduction can impact the reduction of MnO. Previous studies have shown that the formation of initial iron leads to MnO reduction by the dissolved carbon in the metal [18]. The activity of Mn is lower when iron is at the slag/carbon interface, thus increasing the driving force for MnO reduction.

However, the information for the reduction path of MnO and SiO_2 is insufficient and further studies are necessary.

Conclusion

The reduction behavior showed close relationship with raw materials regarding particle size, type of manganese ore and mixture. The results showed that the relationship between particle size and mass loss becomes insignificant when quartz and HC FeMn slag are added into Assmang or Comilog ore. It was thought that considerable amount of incipient slag phase have generated during the early stages of MnO and SiO_2 reduction, which likely diminished the influence of particle size in case of SiMn charges. The mixture type also showed that the reduction behavior becomes similar regardless of ore type when quartz and HC FeMn slag were added into Assmang or Comilog ore during the reduction of MnO and SiO_2. Similar mass losses, which were all relatively very low, were observed with charges samples of As.2, 3 and Com.2, 3 in this study. The already very low a_{MnO} of SiMn charges at 1200 °C shows good accordance of the lower mass losses until rapid reduction. However, the temperatures when the rapid mass loss, which indicates rapid reduction of MnO and SiO_2, begins differed with type of manganese ore and mixture. Comilog seems to have higher rapid reduction temperature than Assmang, and HC FeMn slag and limestone contributes towards lower temperature. However, the reduction path of MnO and SiO_2 needs further investigation. The temperature difference of the rapid reduction was approximately 80 °C when comparing As.3 (1503 °C) and Com.3 (1580-1587 °C). This difference shows indication of possible SiMn production at process temperatures lower than 1550 °C.

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