EFFECT OF CHARGE BASICITY OF TWO COMPOSITIONS ON MnO REDUCTION DURING SMELTING FERROMANGANESE

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The effect of basicity of two different basic charges for reduction of MnO by solid carbon during smelting ferromanganese is considered. The effect of different charge compositions on MnO reduction in the temperature range 1400–1500°C is considered. Experiments are performed in a thermogravimetric furnace in the presence of CO at atmospheric pressure. X-ray spectral fluorescence analysis (XRF) of final slags is conducted with the aim of determining the degree of MnO reduction in relation to charge composition and temperature. It is established that MnO reduction depends strongly on temperature, and charge properties apparently affect reduction insignificantly.

Keywords: ferromanganese, charge, basicity, reduction.

Traditionally high-carbon ferromanganese is produced using carbothermic reduction, which mainly depends on ore chemical and mineralogical compositions, CO reaction capacity, charge porosity, etc. These indices may affect both the process itself and final product quality [1]. Recently results have been published for a number of studies of MnO reduction kinetics during ferromanganese production [2, 3], since this reaction determines the manganese content in final product. However, the effect of charge composition on MnO reduction has not been entirely clarified.

At ferromanganese melting temperatures manganese oxide is reduced to a metal phase by solid carbon according to a reaction

$$MnO\ (l) + C\ =\ Mn\ (l) + CO\ (g) \tag{1}$$

Charge temperature and composition are important factors affecting MnO reduction, which in turn determines the final MnO content in slag.

The degree of MnO reduction from ore of the BHP Company has been studied in [4] using different fluxing additives in the range 1400–1500°C. It has been detected that reduction rate (which depends on the degree of MnO reduction) is very fast with use of charges consisting of BHP ore and limestone, then in a decreasing order follows BHP ore with magnesite, BHP ore with dolomite, and finally the slowest reduction rate corresponds to a charge consisting of BHP ore with fluxing additive.

Reduction of MnO from manganese ore of a deposit in Erzincan in the range 1550–1600°C using slag basicity from 1 to 1.5 has been studied in [5]. It has been established that the degree of MnO reduction by solid carbon increases with an increase in slag basicity.

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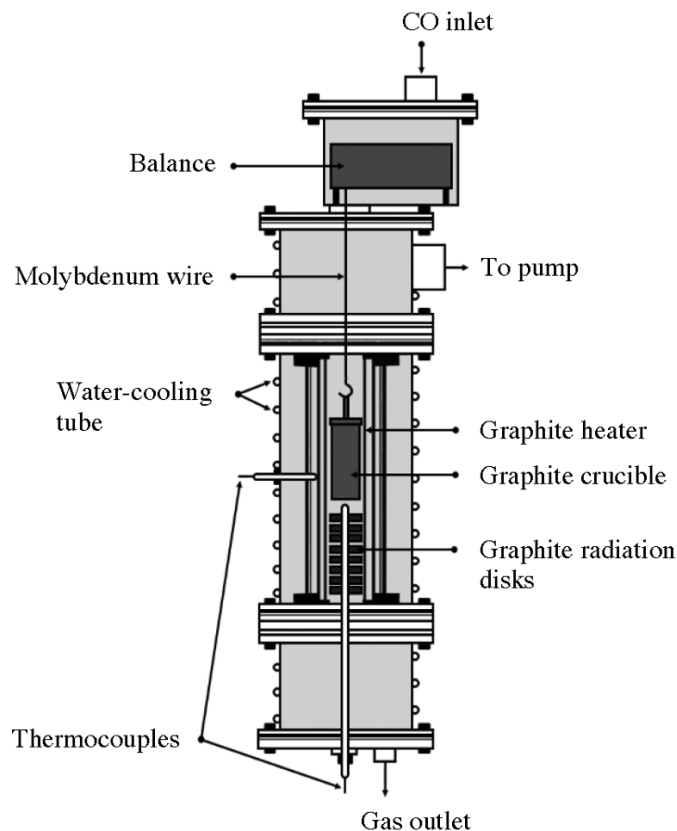
Fig. 1. Layout of thermogravimetric furnace.

In the present study MnO reduction by solid carbon (coke) is examined during production of ferromanganese using two manganese ores, i.e., Assmang and Comilog, by varying the charge composition. The basicity of unfluxed Assmang and Comilog ores comprises 1.3 and 0.04 respectively, and in this case basicity of industrial ferromanganese slag comprised 0.2–1.2, and therefore it was necessary to add lime and quartz to a charge in order to correct basicity to 0.4, 0.5, 0.7, 0.8, and 1.0. Charge basicity was determined in the work as the ratio of overall weight of main oxides (CaO and MgO) to the total weight of acid oxides (SiO_2 and Al_2O_3).

In order to study MnO reduction rate by solid carbon experiments were conducted in a thermographic tube furnace (maximum temperature 1700°C) in which it is possible to record charge weight loss continuously during reduction (Fig. 1).

In the course of experiments specific amounts of manganese ore, lime, quartz, and Polish coke were weighed carefully, mixed manually, and loaded into a crucible and heated to a prescribed temperature. Reduc- tion proceeded with reaction of manganese ore with coke, and in versions with addition of fluxes or without them (depending on the basicity required) in a CO atmosphere. Charge component ratio is given in Table 1. In this case an identical amount of ore was used in each experiment.

With an increase in furnace temperature from room to 500°C a neutral atmosphere was created by adding argon at a rate of 0.5 liter/min. With an increase in temperature from 500°C to the target temperature (1400–1500°C) CO was added to the furnace (instead of argon) at the same rate.

With an increase in temperature to 1200°C the charge heating rate was 25°C/min. A charge was held at 1200°C for 30 min in order to complete all preliminary reduction reactions. Therefore, it is proposed that all iron oxides, and also higher manganese oxides (MnO_x with > 1) are reduced by CO to iron metal and MnO

Table 1. Amount and Basicity of Original Charge Components

Ore in charge	Basicity B					
Asm	1.3	30	–	–	–	7.5
Asm	1.0	30	–	0.45	–	7.5
Asm	0.8	30	–	0.90	–	7.5
Asm	0.5	30	–	3.40	–	7.5
Com	0.04	–	30	–	–	7.5
Com	1,0	–	30	–	7.20	7.5
Com	0,7	–	30	–	5.15	7.5
Com	0,4	–	30	–	2.43	7.5

* Asm is Assmang ore; ** Com is Comilog ore.

Table 2. Ore Chemical Composition from Results of XRF Analysis in which MnO$_2$ Content is Measured by a Titrimetric Method

| Ore in charge	Component content										
Asm	31.4	36.7	15.8	5.14	0.90	0.77	7.10	3.7	0.8	1	103.3
Com	5.23	74.0	3.27	5.50	7.50	0.20	0.27	0.16	4.6	9.85	110.6

Asm and Com correspondingly signify Assmang and Comilog ores.

Table 3. Lime, Quartz, and Coke Chemical Composition

Component	Component content, wt.%										Total
	MnO	Fe$_2$O$_3$	SiO$_2$	Al$_2$O$_3$	MgO	CaO	S	C-fix.	CO$_2$	H$_2$O	
Lime	–	–	1	0.27	1	54	0.01	–	42.3	1	99.6
Quartz	0.14	–	93.9	1.19	0.05	0.09	–	–	–	–	95.4
Coke	0.04	0.86	5.6	2.79	0.22	0.42	0.44	87.7	–	15.5	113.6

respectively [6]. A charge was heated from 1200°C to a prescribed temperature at a rate of 4.5°C/min, which made it possible to model the temperature curve used under industrial conditions. On reaching the prescribed temperature heating ceased, and products after furnace cooling were extracted at room temperature.

Materials used in studies were Assmang and Comilog manganese ores, fluxing additives, i.e., quartz, lime, and also Polish coke, These materials were provided by the Eramet Company in Norway in the form of large lumps. Their chemical composition is given in Tables 2 and 3. Materials were ground separately and screened
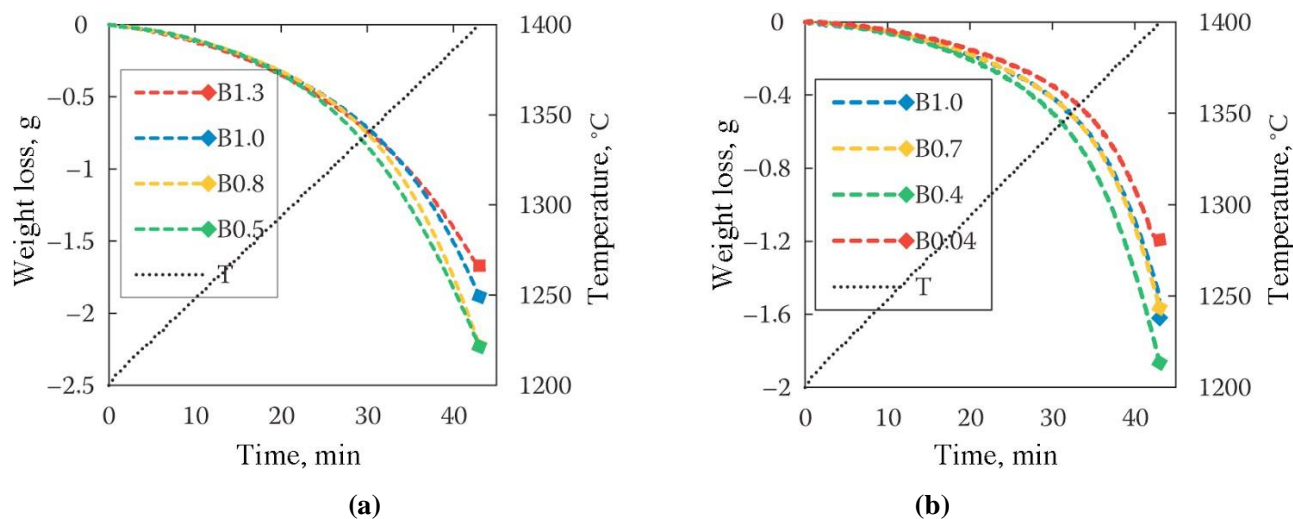
Fig. 2. Reduction curves of Assmang (a) and Comilog (b) charge specimens with different basicity at 1400°C.
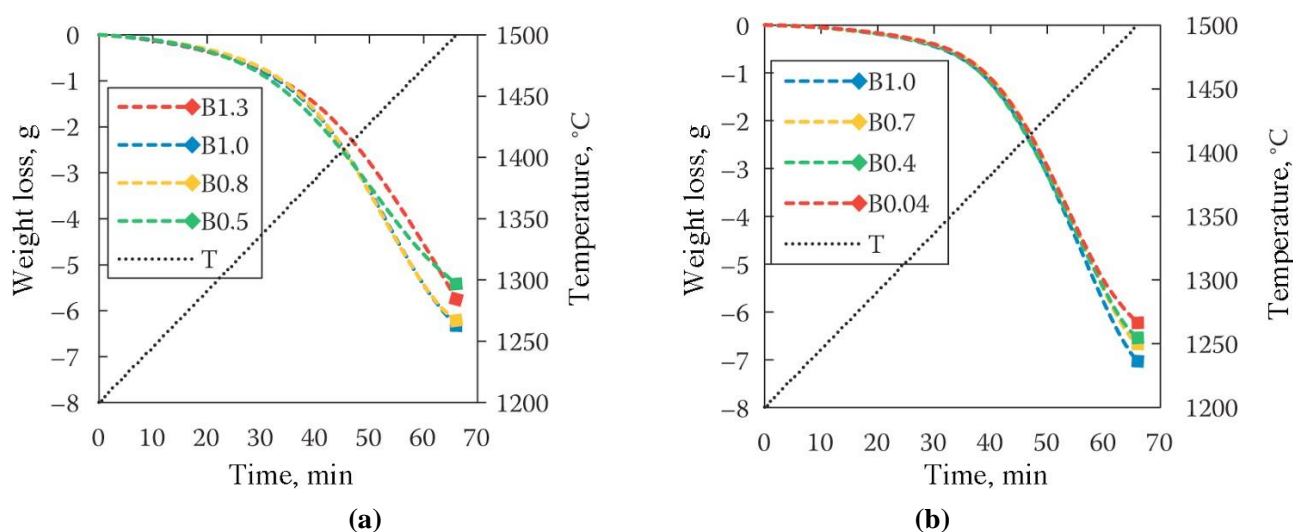
Fig. 3. Reduction curves of Assmang (a) and Comilog (b) charge specimens with different basicity at 1500°C.

with separation of a fraction with a particle size from 0.6 to – 1.6 mm, which was required for the experimental conditions in the thermographic furnace. Then the well-known method of ring and cone quartering was used in order to obtain the most representative selection, and finely ground samples were removed from the test mix for chemical analysis using X-ray spectral fluorescence analysis (XRF), whose results are given in Tables 2 and 3.

It should be noted that the ore used was not dried before reduction. Weight loss was measured during heating in order to determine the degree of MnO reduction. In these experiments only reduction of MnO was determined, and reduction of SiO_2 was not considered since this oxide is more stable than MnO and will not be reduced with the temperature and basicity values used in these experiments. Therefore, it is proposed that any weight reduction is connected solely with MnO reduction. Four different specimens of each ore were studied with heating to 1400 and 1500°C. Weight loss curves were plotted (Figs. 2 and 3). Results show the effect of temperature on MnO reduction of both ores, i.e., weight loss increases with an increase in temperature. Weight

Table 4. Final Slag Chemical Composition

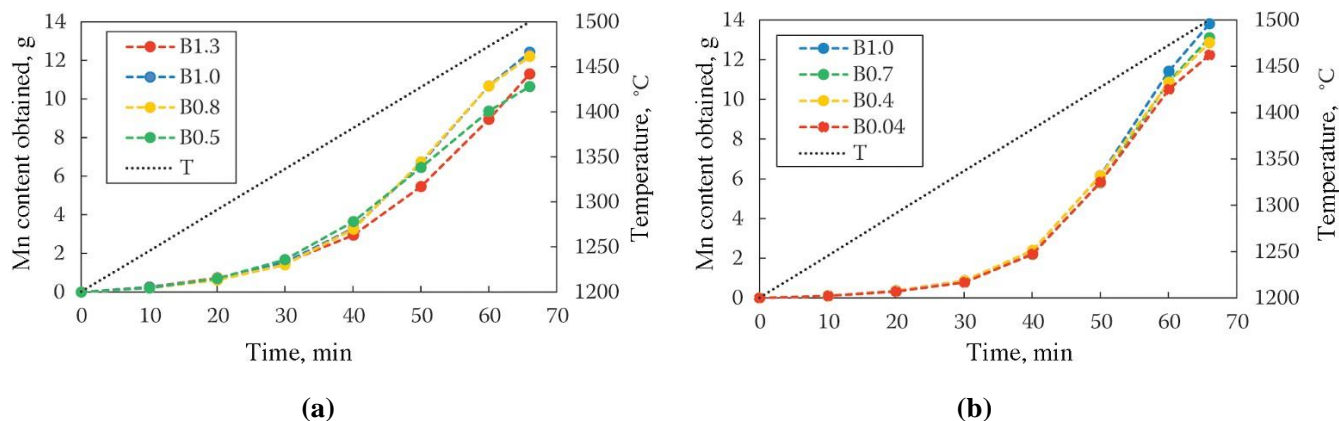| Charge basicity	Compone								
Asm ore				$T = 1500°C$					
B1.3	47.1	18.8	25.5	2.8	3.3	0.2	–	97.7	8.57
B1.0	32.9	26.5	28.5	2.8	4.4	0.2	–	95.3	7.11
B0.8	33.9	30	25.2	2.7	3.7	0.3	–	95.8	7.54
B0.5	37.4	34.5	18.5	2	3	0.2	–	95.6	6.83
Com ore									
B1.0	18.6	17.3	39.3	0.42	22.4	0.09	–	98.0	1.76
B0.7	26.9	16.2	27.7	0.60	26.1	0.07	–	97.6	1.08
B0.4	36.3	19.5	16.4	1.05	16.2	0.08	–	95.1	1.08
B0.04	48.8	20.7	1.00	0.75	28.2	0.10	–	99.5	0.06
Asm ore				$T = 1400°C$					
B1.0	58	11	9.9	0.9	1.6	8.7	4.6	95	6.75
B0.8	57	15	11	0.9	1.5	7.6	4.7	97.7	7.93
B0.5	55	22	11	1.1	1.4	4.3	2.4	97.2	8.64
Com ore									
B0.4	56	8.4	14	0.2	13	1.9	5.4	99.2	1.09

Coefficient $R = CaO/Al_2O_3$.

loss for specimens of Assmang ore vary within the limits $\approx$ 2–6 g with an increase in temperature from 1400 to 1500°C and for specimens of Comilog ore from less than 2 g to approximately 6 g in the same temperature range. An effect may also be observed of adding quartz and lime to a charge, i.e., weight loss increases with an increase in basicity. However, with $T = 1400°C$ weight apparently decreased with an increase in basicity of both ores, and this fact is unexpected and difficult to explain since it does not agree with results of previous re- search [5, 7, 8] in which it was detected that an increase in basicity facilitated MnO reduction.

Slag Composition. In order to determine slag chemical composition an X-ray spectral fluorescence analysis method was used. Results of experiments at 1400°C show (Table 4) a specific level of slag contamination due to presence of iron and some amount of carbon, and therefore they were excluded. Results of experiments at 1500°C were used for conversion of slag compositions and experiments at 1400°C, and also compositions at 1450°C, taking account of the weight loss recorded for determining the degree of residual slag content (Ta- ble 5 and 6).

The Mn content in metal phase for all specimens of Assmang ore increases with an increase both basicity and temperature (Fig. 4a). The sole exclusion is a charge without fluxing additive for which the Mn content in the metal obtained decreases. The calculated content of Mn in metal phase in relation to temperature for a charge with different content of Comilog ore is shown in Fig. 4b. It is seen than Mn content in metal phase

(a)

(b)

Fig. 4. Calculated amount of Mn in the metal phase as function of temperature for all charge specimens with Assmang (a) and Comi-log ore (b).

Table 5. Slag calculated Composition for Assmang Ore in Charge

Charge basicity	T, °C	Com							
	1200	80.9	9.24	1.01	6.79	1.31	0.74	0.04	7.82
Without fluxes	1400	76.5	11.4	1.24	8.34	1.61	0.91	0.05	7.85
B = 1.3	1450	68.1	15.4	1.68	11.3	2.19	1.24	0.07	7.80
	1500	47.1	25.5	2.78	18.7	3.63	1.86	0.05	7.80
	1200	79.6	9.14	0.91	8.41	1.42	0.52	0.00	7.13
Fluxes + quartz	1400	74.3	11.5	1.14	10.6	1.79	0.65	0.00	7.06
B = 1.0	1450	60.5	17.7	1.75	16.3	2.76	1.00	0.00	7.05
	1500	33.8	29.6	2.88	27.2	4.52	1.65	0.00	7.18
	1200	78.2	8.93	0.93	10.0	1.48	0.51	0.00	6.66
Fluxes + quartz	1400	71.3	11.7	1.22	13.1	1.95	0.67	0.00	6.63
B = 0.8	1450	58.2	17.1	1.78	19.1	2.84	0.97	0.00	6.65
	1500	34.5	26.8	2.79	30.0	4.44	1.52	0.00	6.66
	1200	72.1	8.27	0.90	16.9	1.33	0.51	0.04	6.89
Fluxes + quartz	1400	64.2	10.6	1.15	21.6	1.70	0.65	0.05	6.91
B = 0.5	1450	53.3	13.8	1.50	28.2	2.22	0.85	0.07	6.89
	1500	38.5	18.5	1.80	35.2	3.06	1.22	0.10	6.63

increases with an increase in temperature and basicity, reaching a maximum with B = 1.0 as for charges with Assmang ore.

With an increase in basicity the MnO content in slag increases (Fig. 5a), which is caused by the low degree of Assmang ore reduction, and also the small amount of fluxing additive leading to an increase amount of MnO
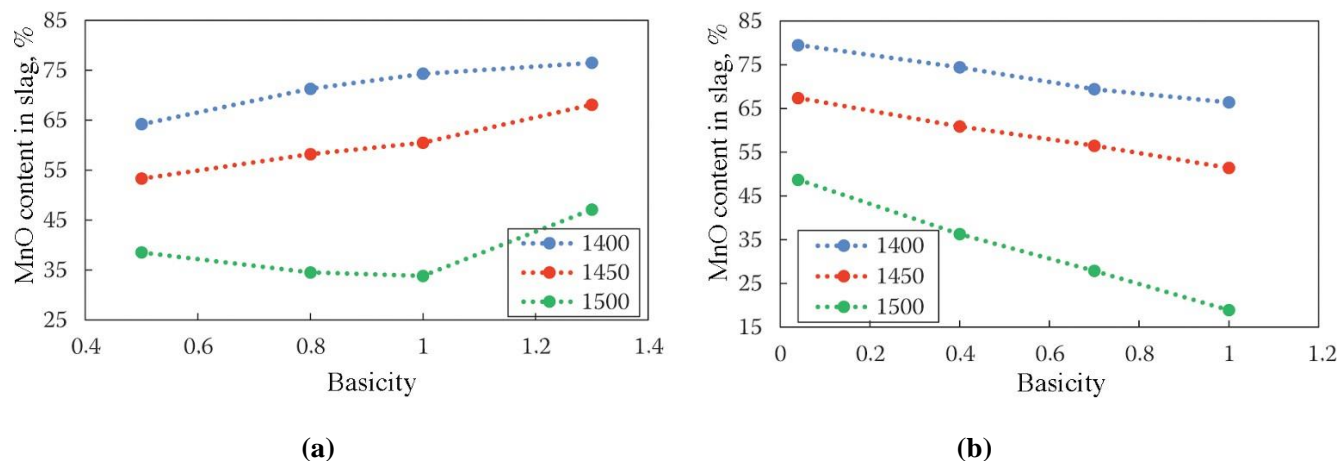
Fig. 5. Calculated MnO content in slag for charge specimens with Assmang ore (a) and Comilog ore (b) of different basicity.

Table 6. Slag calculated Composition for Comilog Ore in Charge

| Charge basicity | T, °C | Component content, wt.% | | | | | | | R |
		MnO	CaO	MgO	SiO_2	Al_2O_3	BaO	K_2O	
Comilog + lime B = 1.0	1200	71.0	14.3	0.14	6.28	8.12	0.14	0.01	1.78
	1400	66.4	16.6	0.17	7.29	9.42	0.17	0.02	1.78
	1450	51.4	24.0	0.24	10.5	13.6	0.24	0.02	1.78
	1500	18.9	39.9	0.44	17.5	22.7	0.40	0.04	1.78
Comilog + lime B = 0.7	1200	74.0	10.7	0.23	6.35	8.49	0.19	0.04	1.29
	1400	69.4	12.6	0.26	7.46	9.97	0.22	0.04	1.29
	1450	56.5	17.9	0.38	10.6	14.2	0.31	0.06	1.29
	1500	27.9	28.7	0.65	16.8	26.1	0.50	0.10	1.12
Comilog + lime B = 0.5	1200	78.3	5.53	0.36	6.64	8.99	0.16	0.02	0.66
	1400	74.4	6.53	0.42	7.84	10.6	0.19	0.02	0.66
	1450	60.9	9.97	0.65	12.0	16.2	0.29	0.04	0.66
	1500	36.3	16.2	1.05	19.5	26.4	0.46	0.05	0.65
Comilog, without fluxes B = 0.04	1200	82.3	0.33	0.25	6.89	9.40	0.21	0.02	0.06
	1400	79.5	0.40	0.30	8.28	11.3	0.25	0.02	0.06
	1450	67.4	0.64	0.48	13.1	17.9	0.40	0.03	0.06
	1500	48.7	1.00	0.75	20.7	28.2	0.63	0.05	0.06

Coefficient R is weight ratio of CaO and MgO to Al_2O_3, since these oxides are not reducible.

is slag. An opposite relationship is observed for charges containing Comilog ore (see Fig. 5b), i.e., with higher basicity the MnO content in slag decreases for greater volumes of slag as a result of fluxing additions. At 1500°C with an increase in basicity the degree of reduction for specimens with Assmang ore is higher, with the exception of basicity of 1.3 with which reduction slows down a little. At 1450°C with an increase in basicity there is also a high degree of Assmang ore reduction (with the exception of basicity of 1.3), although in an experiment with Comilog ore no effect of basicity on reduction was observed.

At 1400°C the reduction capacity for Comilog ore is almost independent of basicity, but reduction of Assmang ore decreases with an increase in basicity. For Assmang ore a relationship in [9] is valid: with low degrees of reduction the reducing capacity decreases with an increase in basicity, but a higher degree of reduction an increase in basicity increases the degree of reduction. For Comilog ore this is also valid with the exception of basicity of 0.04.

CONCLUSIONS

Reduction of MnO in two different charges with solid carbon in CO atmosphere during ferromanga- nese production has been studied. Charge composition and process temperature were varied in experiments. Experiments were performed in a gravimetric tube furnace, which made it possible to record weight loss during reduction.

With a change in temperature in the range 1400–1500°C it has been established that MnO reduction de- pends strongly on temperature. For identical charge compositions (B = 1.0) at 1400°C Assmang ore weight loss is higher than for Comilog ore, and at 1500°C with a corresponding weight loss an opposite result was ob- tained for Comilog ore compared with Assmang ore.

Addition of quartz to a charge of Assmang ore in order to change charge basicity from B = 1.3 to B = 1.0, B = 0.89, and B = 0.5 led to an increase in weight loss at 1450 and 1500°C, and with directly opposite dynam- ics for 1400°C. The same effect has been noted with addition of lime to a charge of Comilog ore for different basicity: B = 0.4, B = 0.7, and B = 1.0. At 1400°C addition of lime to a charge of Comilog ore, apparently not capable of reducing MnO, did not facilitate MnO reduction, and at 1450 and 1500°C it led to an increase in weight loss.

It follows from this that at high temperature MnO reduction increases with an increase in charge basicity. At lower temperature MnO reduction decreases with an increase in charge basicity. This corresponds to results in [9], whose authors established that with a low degree of reduction the amount of solid phase will be greater for higher values of basicity, and for higher values of the degree of MnO reduction the amount of solid phase will increase with an increase in basicity. Exceptions in this work are apparently extreme values of basicity of 0.04 and 1.3 that will always correspond to lower reduction of MnO compared with the trends described above. However, it follows that basicity has a very insignificant effect on MnO reduction.

REFERENCES

1. B. Sorensen, S. Gaal, M. Tangstad, et al., "Properties of manganese ores and their change in the process of calcination," in: *Proc. 12th Int. Ferroalloys Congr. Sustainable Future,* Helsinki, Finland. June 6–9 (2010), pp. 439–448.
2. O. Ostrovski, S. E. Olsen, M. Tangstad, and M. Yastreboff, "Kinetic modelling of MnO reduction from manganese ore," *Can. Inst. of Mining, Metallurgy and Petroleum,* **41,** No. 3, 309–318 (2002).
3. G. Tranell, S. Gaal, D. Lu, et al., "Reduction kinetics of manganese oxide from HC FeMn slags," in: *Proc. INFACON XI* (2007), pp. 231–240.
4. M. Tangstad, *The High Carbon Ferromanganese Process-Coke Bed Relations,* Dr Ing. Dissertation. NTH, Trondheim, Norway (1996).

5. J. R. De Oliveira, E. A. Vieira, D. C. R. Espinosa, and J. A. S. Tenorio, "Influence of temperature, basicity and particle size on MnO reduction," *Mater. Trans.,* **52**, No. 6, 1200–1205 (2011).

6. S. E. Olsen, M. Tangstad, and T. Lingstad, *Production of Manganese Ferroalloys,* SINTEF & Tapir Academic Press. Trondheim (2007).

7. S. E. Olsen and M. Tangstad, "The importance of slag basicity in the production of high carbon ferromanganese," in: Proc. 53rd Electric Furnace Conf. (Orlando, Fl. Nov. 12–15, 1995), Orlando (1995), pp. 93–98.

8. H. Cenginzler and R. H. Eric, *Silicon and Manganese Partition Between Slag and Metal Phases and Their Activities Pertinent to Ferromanganese and Silicomanganese Production,* The Minerals, Metals & Materials Society. Seattle, USA (2016).

9. V. Olsø, M. Tangstad, and S. Olsen, "Reduction kinetics of MnO saturated slags," in: *Proc. INFACON 8,* Beijing, China (1998), pp. 279–283.