IMPROVEMENT OF HIGH-TEMPERATURE ELECTRIC CHARACTERISTICS OF MANGANESE ORES

Y. Miyauchi[1], T. Nishi[1], K. Saito[1] and Y. Kizu[2]

[1]Nippon Denko Co., Ltd., No.62-1, Kohno Tachibana, Anan City Tokushima, Japan.
[2]Nippon Denko Co., Ltd., No.11-8, 2-Chome, Ginza Chuo-ku Tokyo, Japan. E-mail: y-kidu@nippondenko.co.jp

ABSTRACT

At Tokushima Plant of Nippon Denko Co., Ltd. high-carbon ferromanganese is produced by the electric furnace method using lump manganese ores and sintered manganese ores manufactured from fine manganese ores. However, the distribution of manganese ores is significantly uneven on earth, and their characteristics considerably vary by ore type. It is known from experience that the production of high-carbon ferromanganese by the electric furnace method depends greatly on material ores. Therefore, to maintain stable operation in the electric furnace-smelting field, it is important to identify the characteristics of each type of material ores in advance. Thus, we evaluated the high-temperature electric characteristics of manganese ores using the electrical conductivity measuring system developed by ourselves and provided the standards for determining ores and blending ratio necessary for stable operation of the electric furnace based on the evaluation results.

This time we worked for optimisation of the high-temperature electric characteristics of sintered manganese ores through modification of the characteristics because the blending ratio of sintered manganese ores in the electric furnace is high. The electrical conductivity of sintered ores having various chemical components in a high-temperature region (up to 1 550°C) was measured using our electrical conductivity measuring system and high-temperature electric characteristics evaluating method reported at INFACON 9. As the result of the measurement, we revealed that the high-temperature electric characteristics of the sintered ores depend on their chemical contents and the sintered ores can be modified to those having excellent high-temperature electric characteristics by controlling their chemical contents, so that the resources can be effectively used.

1. INTRODUCTION

In recent years, with respect to iron ores used for blast furnaces, it has been identified that properties of materials in the high-temperature region directly influence the productivity and fuel ratio, and studies on softening and melting properties of blast-furnace burden materials are actively carried out using the under load test. On the other hand, similar research has scarcely been done on material ores related to ferroalloys.

In the production of high-carbon ferromanganese using submerged type electric furnaces, the material ore cost and electric power expenses account for the majority of the production cost. Consequently, in Japan with little resources and high electric power unit price, it becomes essential to carry out the operation for maintaining the metal Mn recovery to a high level while the power consumption is kept to a minimal level.

At Nippon Denko, the high-temperature electrical conductivity measuring system was developed, that can evaluate the electrical conductivity of material ores in the high-temperature region. Using this measuring system, the high-temperature electric characteristics of various lump ores were evaluated. Standards were established for determining ores and blending ratio necessary for stable operation by comprehensively assessing the results of a high-temperature electric characteristics test method (previously described at INFACON 9), coupled with evaluation of plant operating performance.

Next, we focused on the high-temperature characteristics of sintered manganese ores. Sintered ores are manufactured on a Dwight Lloyd sintering machine using fine ores and under size (-10 mm) of lump ores. These sintered ores are charged to the electric furnace as part of material ores. Although the blending ratio of sintering material ores needs to be frequently changed depending on the supply situation of material ores, we have been deciding the blending ratio merely taking the sintering characteristics of fine ores and the chemical component of material ores charged to the electric furnace into consideration. However, since the sintered ores including those procured from outside suppliers account for 30 – 50% of material ores charged to the electric furnace, the high-temperature electric characteristics of these sintered ores are estimated to have an important effect on the operation of the electric furnace. For this reason, to achieve greater operating stability of the electric furnace, we worked for optimization of high-temperature electric characteristics of sintered ores.

This report describes the effects of the chemical component of sintered manganese ores charged to the electric furnace on the high-temperature electric characteristics of these ores and the method of modifying their characteristics.

2. EXPERIMENTAL

2.1 Manufacture of sintered ores to be evaluated

To study what effects the chemical component of sintered ores have on their electrical conductivity, we need to evaluate electrical conductivity of each of various sintered ores having different chemical component. Therefore, in the present investigation, sintered ores to be evaluated were manufactured using a small-scale testing equipment to which approx. 5 kg of material ores were charged. Three types of fine manganese ores (-10mm), lime stone (-3mm) and silica (-3mm) were used as material ores and the blending ratio of these ores was changed to modify the chemical component of sintered ores. Table 1 shows the chemical component of sintered ores used in our evaluation.

Table 1. Chemical component of sintered ores used in evaluation.

No.	Mn	Al_2O_3	Fe	SiO_2	CaO	MgO
1	45.0	1.0	5.6	6.4	19.5	3.8
2	43.1	0.94	5.5	11.1	17.9	3.9
3	44.5	3.1	6.0	6.9	16.2	2.3
4	46.9	3.7	5.1	6.3	14.3	1.1
5	47.1	3.2	5.3	6.5	14.3	1.6
6	46.0	4.8	5.1	7.7	14.1	0.8
7	48.5	0.5	5.3	6.8	13.1	3.9
8	46.7	3.4	7.3	6.0	12.7	0.8
9	46.8	4.2	6.0	7.3	12.3	0.9
10	47.4	3.6	5.7	7.1	12.3	2.2
11	48.5	3.8	5.4	6.4	12.1	1.2
12	48.5	3.8	5.4	6.9	11.7	1.6
13	48.0	3.2	7.3	5.8	11.5	1.0
14	45.8	4.8	7.0	8.2	11.0	1.0
15	49.5	3.5	5.9	6.7	10.5	1.3
16	48.2	5.1	5.2	8.0	10.2	0.7
17	49.1	3.6	6.1	7.5	9.9	1.7
18	49.7	3.6	6.0	6.9	9.8	1.7
19	50.5	4.2	5.3	7.1	8.7	0.7
20	50.2	3.6	6.7	6.0	8.6	0.9
21	58.5	4.0	4.1	3.4	0.1	0.3
22	52.4	5.1	5.5	8.2	0.1	0.1

Chemical component is mass%.

2.2 Measurement of electrical conductivity

Figure 1 shows the outline of our electrical conductivity measuring system and Table 2 shows the measuring conditions of apparent specific conductivity.

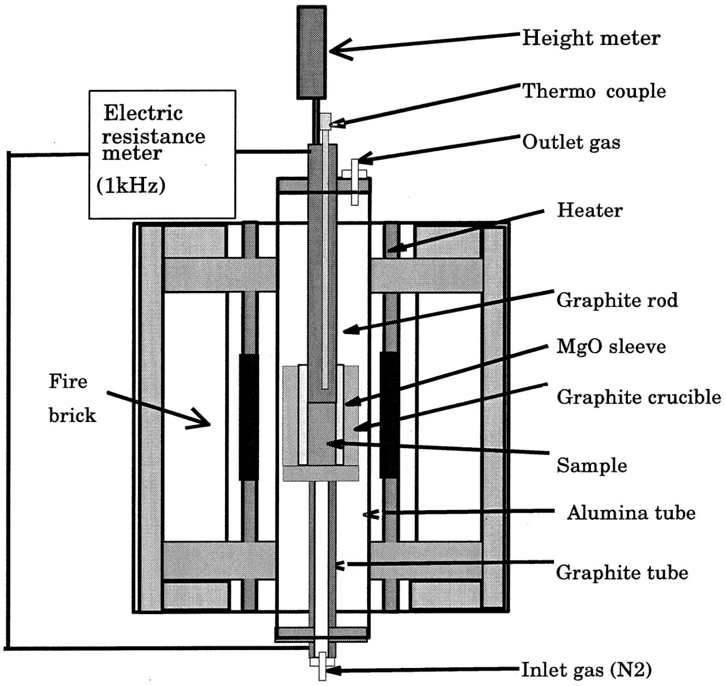

Figure 1. Outline of the electrical conductivity measuring system.

Table 2.Measuring conditions of apparent specific conductivity.

Items	Experimental Condition
Crucible Dia.	Constant
Particle Size of sample	3~5 mm
Bed Height	Constant
Sample Weight	~ 50 g ~
Mixing Ratio of Coke	10%
Particle Size of Coke	3~5 mm
Gas Content	N_2:100%1)
Gas Flow Rate	-
Load	20 kPa
Frequency	1 kHz
Max. Temperature	1 600°C
Heating Rate Room Temp.~800°C 800~1 500°	 10 °C/min 3 °C/min

Nitrogen gas is used for protecting graphite rod and graphite tube.

In the present investigation, we adopted the same conditions we had used when we measured the electrical conductivity of lump ores [1]. In this report, electrical conductivity means apparent specific conductivity obtained by the following procedures.

The specific conductivity referred to here is the apparent specific conductivity obtained by the following procedure. With a predetermined load applied to material ore to be evaluated, electrical resistance (R) and thickness of sample layer (h) are continuously measured while heating, and changes of the apparent specific conductivity (κ) are found from Eq. (1). Similarly, the specific conductivity of carbon-based reducing agent is measured. The behaviours of specific conductivity of these two are compared and material ore is evaluated. The electrical resistance with sample in the blank condition (electrical resistance of the apparatus itself) is negligibly small compared to that of material ore or coke.

$$K=h/(S*R) \tag{1}$$

K : Apparent specific conductivity($\Omega^{-1}cm^{-1}$)
H : Thickness of sample layer(cm)
S : Electrode area(6.25cm^2)
R : Electrical resistance of specimen layer(Ω)

The specific conductivity obtained in the present measurement is not an absolute value. Consequently, in the present method, in order to relatively compare electrical conductivity between ore types, first of all, the apparent conductivity of coke was set as a standard, and the temperature at which the apparent specific conductivity of sample ore to be evaluated exceeded that of coke was designated as the evaluated value. This is explained as follows.

Because the electricity flows preferentially in the section with less resistance as its basic characteristics, the factors that control the electrical resistance of electric furnaces are the half-molten or molten ore and reducing agent (coke bed). What is important from the viewpoint of operating electric furnaces is which would become dominant, and the boundary is the temperature where the specific conductivity of ore and coke bed becomes same. Since a large volume of coke remaining not reacting is observed in the furnace at the time of lowing down the charge level of material, it is apparent that coke bed exists in the electric furnace during regular operation

3. RESULTS AND DISCUSSION

3.1 Apparent specific conductivity of sintered ores

Figure 2 shows the relationship between the apparent specific conductivity of representative sintered ores having different CaO content and temperature. In each case, apparent specific conductivity increases with the rise in temperature. This is linked to the phase change of ore from solid to liquid and when the temperature exceeds 1 200°, it is found that the electrical conductivity of sintered ores varies depending on the CaO content. In the next section, we will discuss electrical conductivity in the high-temperature region, which is influenced not only by the CaO content but also by other chemical component.

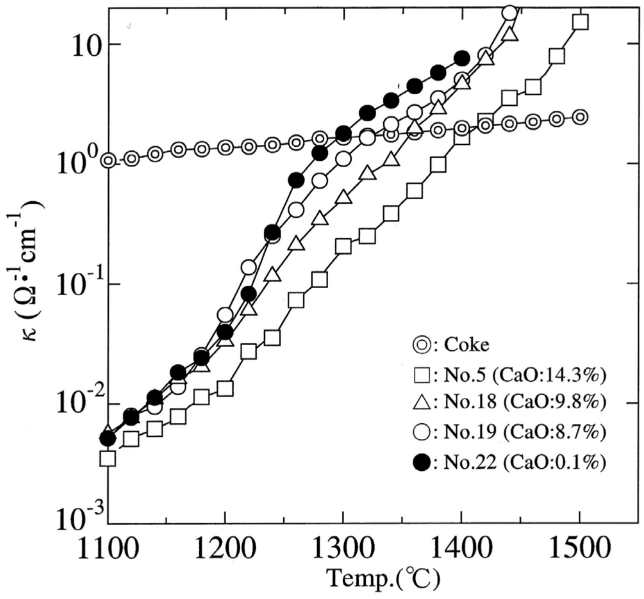

Figure 2. Relationship between the temperature(1 100~1 550°C)
and apparent specific conductivity.

3.2 Chemical component of sintered ores and electrical conductivity

Since the CaO content of sintered ores has an effect on electrical conductivity, we analysed the relationship between the other chemical component of sintered ores and electrical conductivity. The chemical component on which we focused our attention was that of gangue. To be more specific, these are CaO and MgO in the basic component, SiO_2 in the acid component and Al_2O_3 in the neutral component. The gangue reacts with MnO in the softening and melting process and forms molten liquid. The amount of these substances contained as gangue has an effect on the melting point of the molten liquid and the amount of the molten liquid produced. It is generally known that the melting point of the initial melt MnO - SiO_2 and MnO - SiO_2-Al_2O_3 system is 1 251°C and 1 140°C, respectively. Moreover, SiO_2 and Al_2O_3 decrease the softening and melting temperatures of sintered ores. Therefore, these substances are expected to give an effect on electrical conductivity.

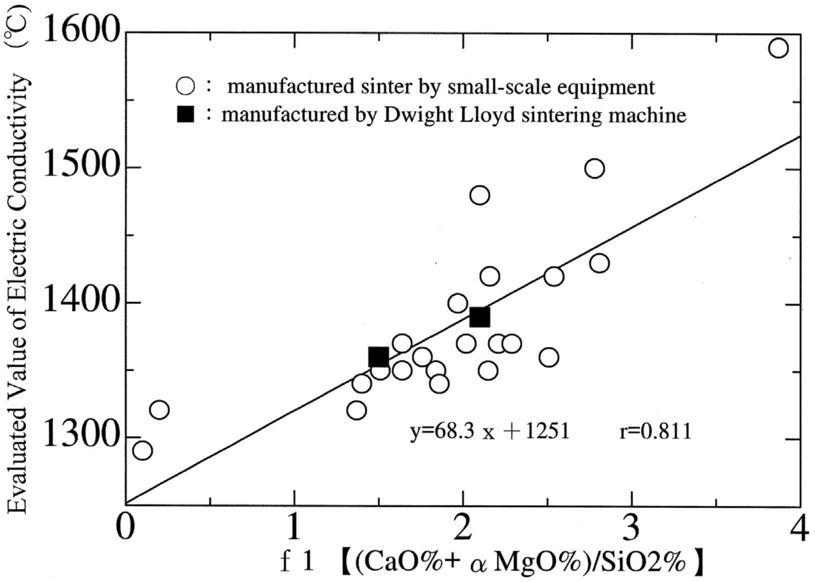

Figure 3. Relationship between the function f_1 of the chemical component and electrical conductivity.

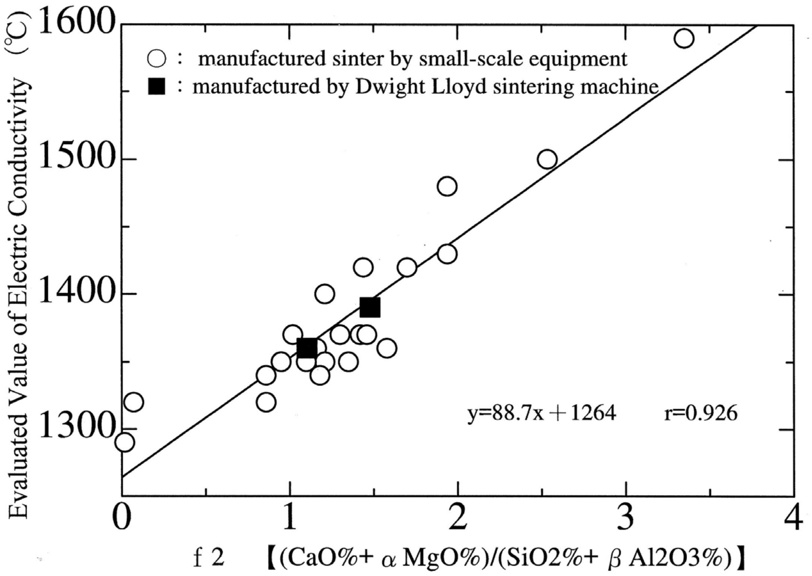

Figure 4. Relationship between the function f_2 of the chemical component and electrical conductivity.

Let us now consider the following function in which CaO, MgO, SiO_2 and Al_2O_3 are the contents of gangue and a%, b%, c% and d% are variables.

$$f_1 = (a+\alpha b)/c \tag{2}$$

$$f_2 = (a+\alpha b)/(c+\beta d) \tag{3}$$

where α,$\beta$are constants.

Figures 3 and 4 show the relationships between the functions f_1 and f_2 of sintered ores and the evaluated values of electrical conductivity (the temperatures at which the apparent specific conductivity of sintered ores exceeds that of coke.) The evaluated values of electrical conductivity tend to increase when the values of the functions f_1 and f_2 are greater. Especially, in Figure 4, in which the effect of the content of Al_2O_3 is taken into consideration, the correlation coefficient obtained by regression is higher as compared to Figure 3 clearly and shows the high correlation. Thus, the chemical component of gangue (CaO, MgO, SiO_2, Al_2O_3) is a major factor controlling the electrical conductivity of sintered ores.

Figures 3 and 4 also show the measured values of the sintered ores manufactured by the sintering machine in our plant. The measurements are mostly on the regression line. Thus sintered ores having any desired electrical conductivity can be produced by modifying the chemical component of these ores using the regression equation shown in Figure 4.

At INFACON9, we reported the following two items as the standards for determining ores and blending ratio necessary for the stable operation of the electric furnace [1].

- The temperature at which the apparent specific conductivity of material ore exceeds the apparent specific conductivity of coke is set as the evaluated value of electric characteristics of the ore, and the ore whose evaluated value is within the range of 1 300°C to 1 500°C is designated as the suitable ore for electric furnace burden.
- The blending ratio of the optimum ore for electric furnace burden of Item 1) above is 80% or more of the total ore charged to the electric furnace

Although there is a clear correlation between the value of the function f_2 and the evaluated value of electrical conductivity as far as sintered ores are concerned, the situation is different for raw ores. We tried to apply the function f_2 to raw ores. As shown in Figure 5, even if the value of the function f_2 is similar for certain ore types, the evaluated values of their electrical conductivity can be significantly different. Therefore, electrical conductivity cannot be determined based only on chemical component. This can be attributed to the fact that the mineral structure of raw ores is largely different depending on the region in which they were mined while that of sintered ores is relatively uniform.

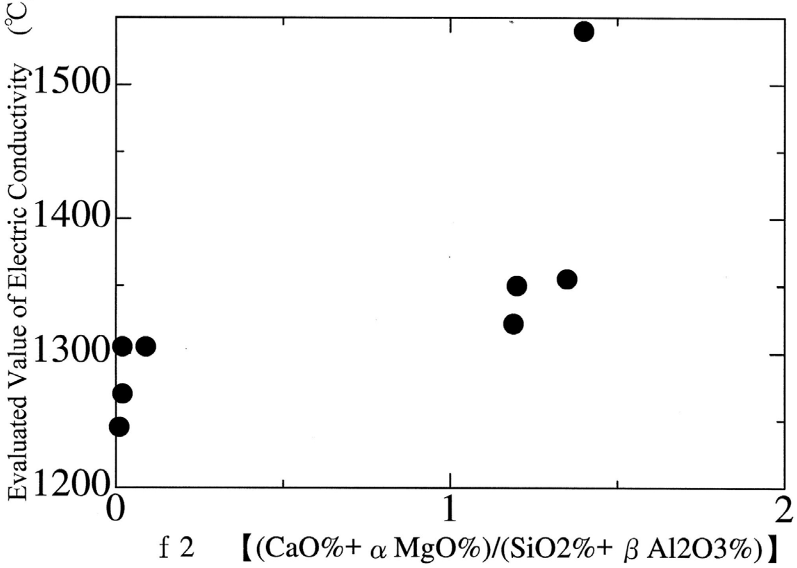

Figure 5. Relationship between the function f_2 of lump ores and electrical conductivity.

In order to maintain the stable operation of the electric furnace, the high-temperature electric characteristics of ores to be charged to the furnace must be kept within an appropriate range even when the available type of raw ores has changed due to the supply situation (i.e.: the ores suitable for charging to the electric furnace should account for at least 80% of the total ores charged to the electric furnace.) The modification of the high-temperature electric characteristics of sintered ores is an effective method for achieving this objective. By modifying the chemical component of gangue within the suitable range, sintered ores suitable for charging to the electric furnace can be manufactured. Thus, the blending ratio of ores suitable for charging to the electric furnace can be increased.

3.3 Results of the analysis of electric furnace operating performance

Based on the findings obtained in these experiments, we analysed the past operating performance of the electric furnace. Table 3 shows the performance in Periods I, II and III during which the value of the function f_2 of sintered ores was significantly changed.

Table 3. Operating performance of electric furnace and material ores.

			Operating period		
			I	II	III
(blending ratio of ores)					
Raw ores	Suitable ores 1)		45.1%	59.7%	51.4%
	Unsuitable ores 2)		17.8%	5.0%	13.6%
Sintered ores	The value of f_2 3)				
	A	0.72	19.0%	9.9%	0.0%
	B	0.09	0.0%	11.3%	20.0%
	C	2.70	18.1%	14.1%	15.0%
(Operating performance)					
Slag basicity ($CaO\%/ SiO_2\%$)			0.93	0.92	0.92
Mn content of slag 4)			100	104	106
Electric power consumption 4)			100	101	103

1) Ores with the evaluated value of electrical conductivity within the range of 1 300 – 1 500°C.
2) Ores with the evaluated value of electrical conductivity not within the range of 1 300 – 1 500°C.
3) Chemical component of sintered ores $(CaO+\alpha MgO) / (SiO_2+\beta Al_2 0_3)$
4) The operating performance (in terms of Mn content of slag and electric power consumption) in Periods II and III are compared with that in Period I which is set at 100.

The electric furnace was operated in the normal mode during Period I. During this period, two types of sintered ores were used, the values of the function f_2 of which were 0.72 and 2.70 respectively. The evaluated value of electrical conductivity of these sintered ores was considered to be within the suitable range and operating performance was satisfactory.

During Period II, the operating condition of the electric furnace was good as it was in Period I and electric power consumption was almost the same. In this period, sintered ores having an extremely low value of the function f_2 accounted for 11% of the total material ores used. Although the evaluated value of electrical conductivity of this ore is considered not to be in the suitable range, good furnace operating performance could be maintained because the percentage of the ores suitable for charging to the electric furnace exceeded 80% of the total material ores used (meeting the standards set forth in Section 3.2 above.)

Then it shifted to Period III. The gas temperature in the furnace gradually increased, thermal efficiency declined and electric power consumption deteriorated during this period. The percentage of sintered ores with a low value of the function f_2 was 20% of the total material ores used, moreover, that of raw ores with the evaluated value of electricity conductivity not within the suitable range reached 14%. As a result, the percentage of ores suitable for charging to the electric furnace declined to 66% and this could have caused operating performance to fall. The operating performance (in terms of Mn content of slag and electric power consumption) in Periods II and III are compared with that in Period I which is set at 100.

Based on the comparison of above-described operating performance, the suitable range of the value of the function f_2 of sintered ores is considered to be 0.7 – 2.7. Moreover, it would be desirable that the percentage of both raw and sintered ores suitable for charging to the electric furnace exceeds 80% of the total ores charged to the electric furnace.

4. CONCLUSION

The distribution of manganese ores is significantly uneven on earth and, as shown in Figures 2 and 5, their high-temperature electric characteristics considerably vary by ore type.

In order to maintain the stable operation of the electric furnace, the high-temperature electric characteristics of ores to be charged to the furnace must be kept within an appropriate range even when the available ore type of raw ores has changed due to the supply situation (i.e.: the ores suitable for charging to the electric furnace should account for at least 80% of the total ores charged to the electric furnace). The modification of the high-temperature electric characteristics of sintered ores is an effective method for achieving this objective.

Adding the findings obtained in the above-described investigations, we modified the standards for determining ores and blending ratio necessary for stable operation of the electric furnace that were initially reported at INFACON9.

The changed standards are as follows:

- The temperature at which the apparent specific conductivity of material ore exceeds the apparent specific conductivity of coke is set as the evaluated value of electric characteristics of the ore, and the ore whose evaluated value is within the range of 1 300°C to 1 500°C is designated as the suitable ore for electric furnace burden.
- Sintered ores with the chemical component [CaO(a%), MgO(b%), SiO_2(c%), Al_2O_3(d%)] that have the value of the function f_2 $[(a+\alpha b) / (c+\beta d)]$ within the range of 0.7 – 2.7 are suitable for charging to the electric furnace. When manufacturing sintered ores, their chemical component needs to be modified to show the value of the function f_2 within this range.
- The blending ratio of the optimum ore for electric furnace burden of Items 1) and 2) above is 80% or more of the total ore charged to the electric furnace

The above-described renewed standards have been established taking only the high-temperature electric characteristics of ores into consideration. We needed to further improve the operating stability of the electric furnace by investigating the effects of other factors.

5. REFERENCES

[1] Yoshihiro MIYAUCHI et al., High Thermal Electric Property of Manganese Ore in Production of High Carbon Ferromanganese, INFACON9, Quebec City, Canada, 2001, 236-243.