

Optimization of Conditions to Produce Manganese and Iron Carbides from Denizli-Tavas Manganese Ore by Solid State Reduction

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Abstract

In this work, optimization of conditions in the production of manganese-iron carbides from Denizli-Tavas manganese ore by solid state carbothermic reduction in argon atmosphere has been investigated. The ore was calcined and then mixed with active carbon and CaO. Experiments were performed in a horizontal tube furnace that can be heated up to 1700 °C with MoSi₂ heating elements. The optimized parameters were; temperature, time, carbon percentage, and CaO percentage. After each experiment, weight loss data were obtained and converted to percentage reduction.

Key words: Solid state reduction, manganese carbide, iron carbide.

Introduction

Manganese is an element with numerous applications in industry. Roughly 95% of all manganese products in the world are used in iron and steel production nowadays and the remaining part is used for the production of dry cell batteries and also for certain chemical aims. In the future manganese and its alloys are expected to be used in a variety of applications such as low cost shape memory alloys, low cost stainless steels, manganese stainless steels, and high-speed transportation.

Manganese is used widely in metallurgy as desulphurizer, mild deoxidant, pearlite refiner, ferrite toughener, etc. for hardenability and in Hadfield steels. It is used principally in combination with silicon for deoxidation of steel. Some 30% of the manganese is still used for these 2 main properties today.

The other 70% of manganese is used purely as

an alloying element for steels. It lowers the temperature at which austenite transforms into ferrite, thus avoiding cementite precipitation at ferrite grain boundaries, and by refining the resulting pearlitic structures, it gives rise to ferrite formation. Therefore, it increases the hardenability of steel and gives higher strength and better toughness. Steels containing 10%-14% manganese are known as 'Hadfield Steels' and are extremely hard and tough. Another important property of manganese, like nickel, is its ability to stabilize austenite in steel. It is not as powerful as nickel to achieve this effect but it has an advantage of being much less expensive. Manganese also increases the work hardening rate, thus improves mechanical properties.

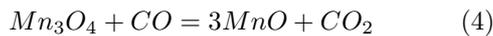
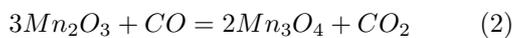
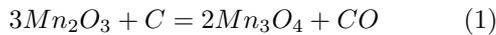
Chemically pure manganese is obtained by reducing manganese oxides with alkaline metals or with calcium and magnesium. In addition, there is an electrolytic method of producing pure manganese. When manganese oxides are reduced by hybrids of

alkaline-earth metals, it is possible to obtain metal manganese containing 99.999% Mn (Olsen et al., 2007).

Ferromanganese is defined as an alloy of iron that contains a sufficient amount of manganese to be useful as an agent for addition into molten metals, usually steel, and today blast furnace and electrical furnace are 2 main methods in the production of ferromanganese. Blast furnace production is very similar to pig iron production in blast furnace, but structurally the only difference is that the shaft height is lower in the ferromanganese blast furnace. The main difference in process is that the iron oxides are reduced in the shaft of the furnace whereas manganous oxides are reduced in the bosch and hearth regions at higher temperatures. In electrical furnace production, 2 processes, high manganese slag process and low manganese slag process, are employed. Furnaces should be closed in order to prevent atmospheric pollution with high electrical and metallurgical efficiencies. Furthermore, an efficient gas cleaning system is necessary to remove fume and dust from the furnace gases.

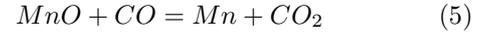
The reduction of manganese oxides can be investigated in 2 stages; reduction of higher manganese oxides and reduction of manganous oxide. Mn_2O_3 , Mn_3O_4 , MnO_2 , and MnO are known oxide forms of manganese in nature.

MnO_2 transforms into lower oxide phases under suitable condition of temperature and oxygen partial pressure. The gaseous reduction of higher manganese oxides starts with the dissociation of MnO_2 into manganic oxide above 400 °C and continues with the reduction of the oxides Mn_2O_3 and Mn_3O_4 in the Mn-C-O system with the support of reducing agents such as carbon and carbon monoxide with respect to the reactions below;



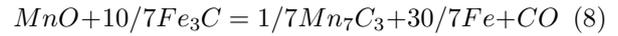
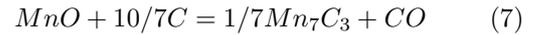
The possibility of the reduction of MnO_2 to MnO at a temperature below 500 °C in a CO atmosphere is proved by Pentz (1970) but the product is unstable after cooling and may reoxidize when exposed to air. Pentz (1970) and Yagihashi et al. (1963) have shown that in order to reduce MnO_2 to stable MnO when cooled, the reducing temperature has to be above 700 °C.

MnO is a stable oxide. After the reduction of high manganese oxides to MnO , very high pressures of CO is required to continue the reduction reactions with CO. The reduction of MnO can be presented with reactions given below;



Several researchers such as Bouchard and Fruchart (1964), and Tanaka et al. (1973) have studied the thermodynamics and phase equilibria of manganese oxides and indicated that the possible manganese carbides are $Mn_{23}C_6$, $Mn_{15}C_4$, Mn_3C , Mn_5C_2 , and Mn_7C_3 .

According to Grimsley et al. (1977) the reduction of MnO by CO is thermodynamically impossible in the range of 25 °C to 2000 °C. Nevertheless, the reduction preferentially takes place by solid carbon or iron carbides with respect to the equations below;



The standard free energy changes for reduction of MnO with carbon and Fe_3C are almost identical in the temperature range between 800 °C and 1300 °C and the most likely product is Mn_7C_3 .

Kalfaoglu (1997) studied the solid state reduction behavior of Denizli-Tavas manganese ore to produce ferromanganese using pure carbon as graphite. He collected weight loss data with respect to time as the reactions took place in the furnace. Experiments were done at 1100, 1150, 1200, 1250, and 1300 °C and a constant amount of carbon and calcined manganese ore were used for each experiment. Reactions were allowed to take place in an argon atmosphere inside the furnace in order to prevent oxidation. From experimental results, it was seen that approximately 60% reduction of the manganese ore took place at and below 1200 °C. At and above 1250 °C, it was observed that this reduction efficiency increased up to approximately 90% and it was deduced from his study that it was possible to produce Fe-Mn alloy from the Denizli-Tavas manganese ore by solid state reduction with carbon.

Main purpose of this study was to find the optimum conditions to produce a charge material for the ferromanganese production or steelmaking with high content of iron and manganese carbides from Denizli-Tavas manganese ore by carbothermic reduction and understand the effects of temperature, time, carbon addition, and CaO content on this reduction.

Experimental Procedure

Method used in the experiments was reducing the Denizli-Tavas manganese ore with active carbon and using CaO as a binder under argon atmosphere in a horizontal tube furnace using alumina crucibles. Experimental procedure involved the reduction of the Denizli-Tavas manganese ore with active carbon, and the use of CaO as a binder under argon atmosphere in a horizontal tube furnace using alumina crucibles.

In a muffle furnace, 250 g of Denizli-Tavas manganese ore was calcined at 1000 °C for 2 h. The aim of calcination of this ore was to increase its manganese content and eliminate CO₂. The sample was mixed by a riffle 3 times in 1 h calcination time to obtain uniform oxidation. The sample weight was 210 g after calcination and corresponding mass loss was as 16%. The composition of both calcined and uncalcined ore samples are given in Table 1.

Table 1. Composition of Denizli-Tavas manganese ore.

Components	Uncalcined (wt. %)	Calcined (wt. %)
Mn	31.06	39.69
Fe	4.26	5.45
SiO ₂	13.54	17.30
CaO	7.45	13.41
MgO	0.86	1.10
Al ₂ O ₃	2.46	3.14

X-Ray diffraction analysis of the calcined manganese ore was conducted at the Department of Metallurgical and Materials Engineering at METU. Results can be seen in Figure 1.

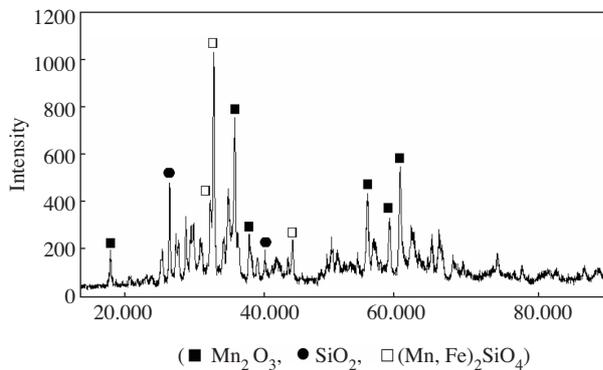


Figure 1. X-Ray diffraction analysis of calcined ore.

Experiments were performed in a tube furnace, made in England by Lenton Co., which was designed

to work at temperatures up to 1700 °C with the work tube made of 99.80% recrystallized alumina. A schematic view of the furnace can be seen in Figure 2.

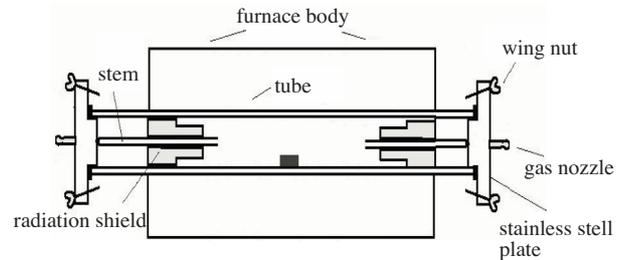
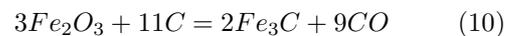
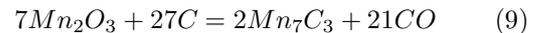


Figure 2. Schematic view of the furnace.

Calibrations of furnace temperatures were performed at temperatures of 1400, 1500, and 1600 °C using Pt/Pt-10%Rh thermocouple taking measures at each 28 points in the central region of the furnace. The temperature at the central part (4 cm distance) of the furnace was constant within ± 1 °C. Crucibles were placed in this interval in all experiments. Calibration line of set temperature versus actual temperature was also drawn.

The flowmeter was originally calibrated for air, so it was recalibrated for argon. In the experiments, argon flow rate was kept constant at 25 cc/min.

After calibration of furnace temperature and flowmeter, carbon requirement calculations were made, and total weight of calcined ore and carbon was adjusted to 50 g. Carbon requirement calculations were made according to reactions (9) and (10) given below.



Chemically pure active carbon was used in the experiments in very fine powder form as a reducing agent and commercially available CaO in powder form with a 99.9% grade was used in all of the experiments.

The charge consisted of 43.27 g of ore and 6.73 g of active carbon. Calcium oxide was added as binder and flux as 5% of the ore. This mixture composition was used in temperature and duration optimization experiments but calcium oxide and active carbon quantities were changed in other experiments in order to determine the optimum conditions. All of the charge material was mixed and ground with the addition of alcohol in a ceramic mortar and after all

the alcohol vaporized off, it was put into the alumina crucibles.

Experiments were conducted by placing the 3 alumina crucibles into the predetermined 4 cm interval inside the furnace. Different temperatures, durations, and active carbon and calcium oxide percentages were tested in order to find the optimum conditions for carbothermic reduction of Denizli-Tavas manganese ore. After each experiment, weight loss of the crucible and contents was measured and converted to reduction percentage.

Reduction percentage, defined as the weight loss of ore during the reduction with carbon, after a certain period of time at a given temperature was expressed as the percentage of the total weight loss for complete reduction of the ore.

The weight loss was converted to percentage reduction, R%, using the following formula;

$$R\% = \frac{\text{Mass of Oxygen Removed}}{\text{Mass of Removable Oxygen}} \quad (\text{Eq.1})$$

Mass of oxygen removed in the above formula was the weight loss while mass of removable oxygen was the oxygen present in the reducible oxides in the system. Fe oxides and Mn oxides were considered to be the reducible oxides and all other oxides were classified as non-reducible in the calculation of R%.

Experiments were done using combinations of the parameters given in Table 2 below. The optimum reducing conditions were tried to be established.

Results and Discussion

The experimental results of the eleven experiments performed are shown in Table 3.

Effect of temperature

The reduction process was performed while changing temperatures at constant time intervals, with 100% of the stoichiometric amount of carbon and with CaO addition, which is 5% of the ore under argon atmosphere. Temperatures studied were 1150, 1200, and 1250 °C. In these experiments, time was kept constant at 2 h.

Percentage reduction values calculated with respect to the temperatures in these tests are 47.1%, 56.42%, and 70.31%, respectively. It can be seen from these results that % reduction increases with increasing temperature. Results of these 3 experiments are given in Figure 3.

The reason for relatively low reduction can be explained by the fact that certain reduction reactions or mechanisms do not occur below a certain temperature. Also the results indicate that complete reduction was not obtained in the experiments in

Table 2. Experimental variables.

<i>Variable</i>	<i>Range</i>
Temperature (°C)	1150 – 1200 – 1250
Duration (h)	2 – 4 – 5 – 6
Stoichiometric Carbon	100% - 150% - 200%
CaO Percentage	2.5% - 5% - 7.5% - 10%

Table 3. Results of the experiments.

Exp.	Temperature (°C)	Duration (h)	CaO (%)	Stoich. Carbon (%)	Reducibility (%)
1	1150	2	5	100	47.10
2	1200	2	5	100	56.42
3	1250	2	5	100	70.31
4	1250	4	5	100	83.85
5	1250	5	5	100	85.75
6	1250	6	5	100	87.72
7	1250	4	5	150	68.54
8	1250	4	5	200	70.88
9	1250	4	2.5	100	64.78
10	1250	4	7.5	100	65.37
11	1250	4	10	100	69.61

2 h and maximum reduction percentage obtained was 70.31% at 1250 °C. Since temperatures above 1250 °C cause partial melting in the mixture and sticking into the walls of alumina crucible higher temperatures were not used and 1250 °C was taken as optimum.

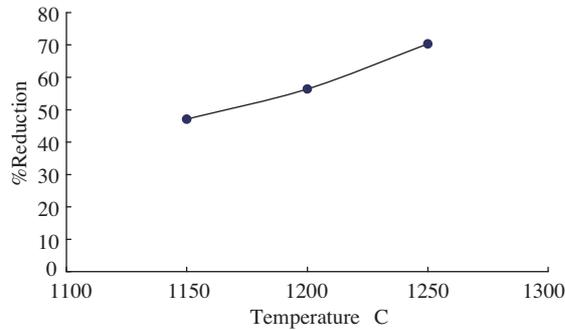


Figure 3. % Reduction versus temperature graph (100% stoichiometric amount of carbon, 5% CaO addition, 2 h).

Effect of duration

In order to determine the effect of duration, 3 experiments were conducted at 1250 °C for 4, 5 and 6 h using 100% of the stoichiometric amount of active carbon and CaO addition which is 5% of the ore. The variation of reduction % with time is given in Figure 4.

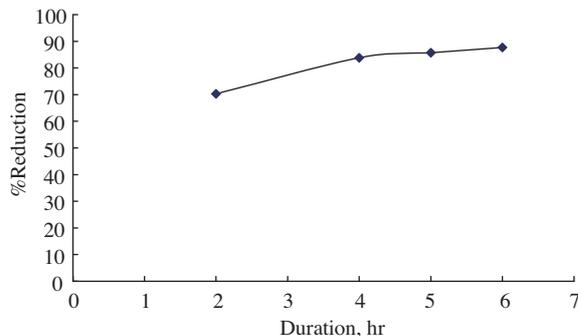


Figure 4. % Reduction versus duration graph (100% stoichiometric amount of carbon, 5% CaO addition, 1250 °C).

Table 3 shows that reduction percentage values calculated increased from about 70% to about 88% as the time changes from 2 to 6 h. In the reaction system, iron oxides and manganese oxides were reduced by active carbon and the reduction extent of oxides was found to depend very much on reduction time.

As mentioned in previous studies (Kalfaoğlu, 1997), among these oxides, iron oxide was the least stable one and it was almost fully reduced in a time less than 1 h. On the other hand, reduction of MnO was not completed even at the end of 3 h but as reduction preceded, reduction extent of manganese oxides increased. Furthermore, according to the study of Kalfaoğlu (1997), increase in the duration gave better reduction percentage values and results of this study are in accordance with it.

Effect of excess carbon

Experiments were also performed with 150% and 200% of the stoichiometric amount of carbon calculated for reactions (9) and (10) in order to determine its effect on % reduction while keeping the temperature at 1250 °C for 4 h.

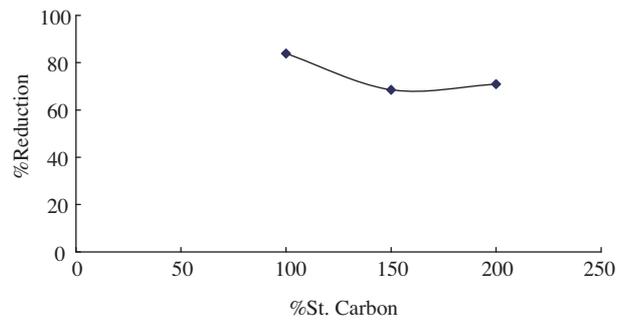


Figure 5. % Reduction versus stoichiometric amount of carbon graph (5% CaO addition, 1250 °C, 4 h).

As shown in Figure 5, the reduction percentage decreases from 83.85% down to 68.54% when the amount of carbon increases from 100% up to 150% and then slightly increases up to 70.88% when the amount increases up to 200%. Therefore it is clear that it was not necessary to use excess carbon.

Emeksiz (1991) stated in his work that excess coke used in a smelting experiment for which coke/ore weight ratio of 0.3 was observed at the end of experiment to form a layer above the slag. This coke layer was also found to contain significant quantities of metal and slag beads, which have not been able to settle down into the slag and metal phases lying below. This resulted in a decrease in the weight of the metal formed causing a decrease in the manganese recovery. With respect to this situation, when excess of stoichiometric amount of active carbon was used in reduction of Denizli-Tavas manganese ore, a

Table 4. Results of the test carried out with the optimum conditions.

Composition of Product (wt. %)							Reduction %	
Mn	Fe	Ca	Al	Si	Mg	K		C and O
52.98	5.62	7.10	2.10	8.60	0.82	0.44	22.33	%83.85

carbon layer might have formed inside the product which decreased the reduction percentage.

Effect of CaO %

To understand the effect of the CaO amount in the charge, 3 tests were carried out with 2.5%, 7.5%, and 10% CaO addition using 100% of the stoichiometric amount of active carbon at 1250 °C. The results are shown graphically in Figure 6.

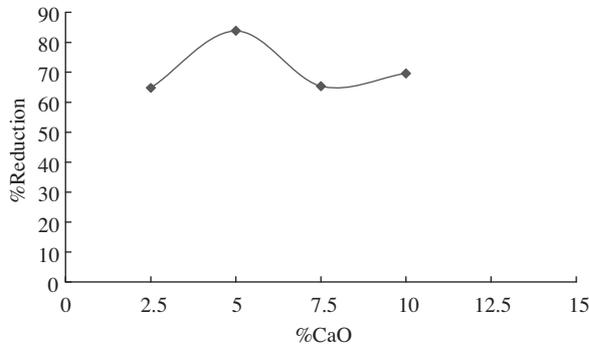


Figure 6. % Reduction versus CaO% addition graph (100% stoichiometric amount of carbon, 1250 °C, 4 h).

It can be deduced from the results that the optimum value for CaO addition is 5% and the amounts higher or lower than this give low reduction percentages. The reason for this may be that CaO helps as binder up to 5% in the charge, but it hinders carbide formation above that value.

Optimum conditions

Considering the experimental results, the optimum conditions found for the reduction of Denizli-Tavas manganese ore were 1250 °C, 4 h, 100% of stoichiometric amount of active carbon, and 5% CaO addition. Under optimum conditions, 83.85% reduction of calcined ore was obtained. Under these conditions, a test was carried out and a product with composition shown in Table 4 is obtained. Comparing the composition of the present product with calcined ore composition in Table 1, it is seen that Mn-content of product increased from about 40% to about 54%.

XRD analysis of the product, which was obtained in optimum conditions, is given in Figure 7.

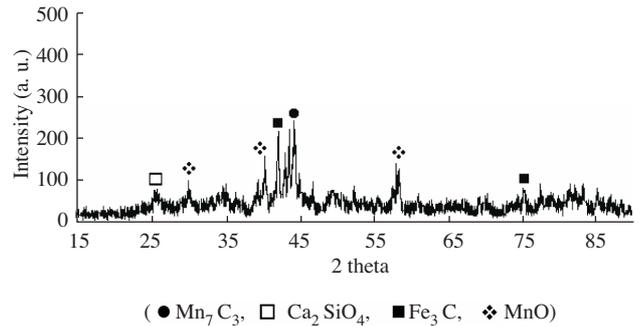


Figure 7. X-Ray diffraction analysis of the product produced under the optimum conditions.

Conclusions

In this research, the optimization of conditions to produce iron and manganese carbides from Denizli-Tavas manganese ore was studied. The following conclusions were drawn considering the experimental results:

1. To obtain a high reduction percentage, temperature should be as high as possible to a point at which partial melting of the charge starts to occur. Utilizing 1250 °C as the reduction temperature was found to be advantageous since it ensures a high reduction percentage, and keeps the charge completely at solid state.
2. From the energy consumption and high reduction percentage points of view, 4 h reduction time was found to be advantageous since further increment in duration does not provide a significant change in reduction percentage.
3. In order to obtain satisfactory reduction percentage, it was not necessary to utilize active carbon in excess of the stoichiometric amount. Amounts higher than 100% of the stoichiometric amount of active carbon decreased the reduction percentage values.

4. Presence of calcium oxide in the charge was found to be beneficial for the reduction and helps as a binder up to 5 wt. %, but it prevented carbide formation and decreased the reduction percentage above that value.

Prereduction of the manganese ore prior to smelting offers several advantages over direct smelting such as increased manganese recovery, less carbon

requirement for smelting, and therefore the overall operation and slag viscosity are easily controlled and more oxygen and volatile matter are removed prior to smelting.

Since the manganese content of the ore product increased under the optimum conditions, the product obtained in this study can be used for ferromanganese production.

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