MECHANISM OF CARBOTHERMIC REDUCTION OF Mn OXIDE POWDER

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ABSTRACT

In the carbothermic reduction of Mn oxides powder, Mn oxides higher than MnO are reduced to MnO at temperatures less than 1150°C. As temperature continues to increase beyond 1150°C, MnO reacts with carbon to form Mn_7C_3 until temperature reaches to about 1300°C. As it is not stable at about 1300°C or higher, Mn_7C_3 dissociates into Mn alloy melt and carbon, which is dissolved in Mn alloys. As temperature increases further, a remnant MnO after forming Mn_7C_3 is reduced by carbon.

KEYWORDS: *Mn oxides, carbothermic reduction, Mn_7C_3, XRD analysis.*

1. INTRODUCTION

The production of Mn alloys has been designed and practiced on the base of carbothermic reduction of Mn oxides, and the carbothermic process of Mn oxides is expected to continue as the principal smelting mode of Mn alloys in a foreseeable future. Olsen et al. [1] presented well the status and issues of the processes as practiced by the industry of Mn alloys. At present, with ever increasing awareness of needs for the conservation of natural resources, the practitioners in the community of Mn alloys raise a concern on the sustainability of the business and are challenged to improve and/or develop processes with enhanced efficiencies. A greater gain would be realized from the efficient carbothermic smelting process. Therefore, a further improvement of the process requires a good understanding of the mechanism of carbothermic reducing reaction of Mn oxides.

In this study, experiments for carbothermic reaction at various temperatures were carried out with composite pellets prepared with the mixture of Mn oxides and graphite powder. The experimental results were analyzed and discussed to determine the mechanism of reactions involving Mn oxide powder and graphite.

2. EXPERIMENTS

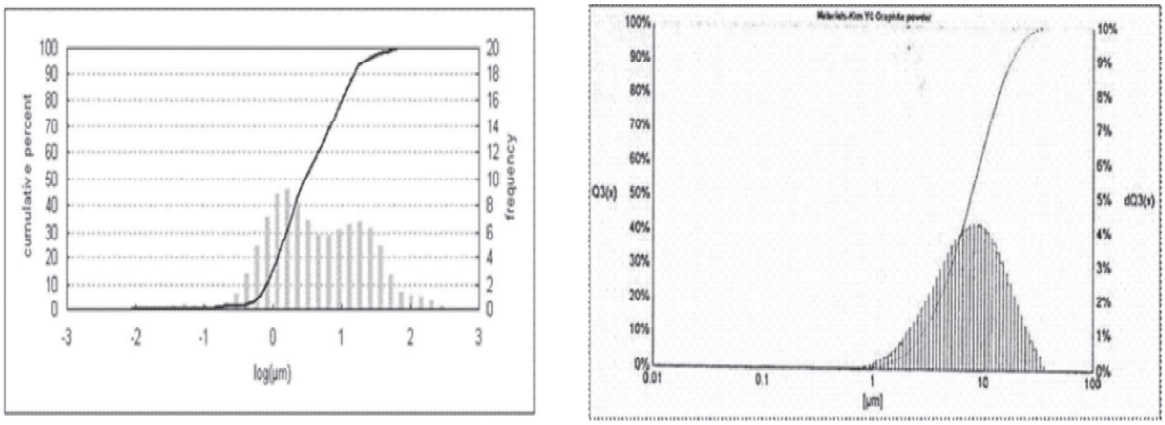
This experiment is designed to study reaction of Mn oxide and carbon powder at high-temperatures. The samples are prepared with high purity Mn oxide and graphite powder to maximize interface. To provide an intimate contact they are mixed and pressed into pellets.

2.1. Raw materials

By-product collected from the refining process of MC and LC FeMn alloys is a high purity Mn oxide powder. Its chemical composition is shown in table 1. Its Mn content is 66.83 %. It is found to be in the form of Mn_3O_4. Its content is 92.76 % in Mn oxide powder. Its analyzed particle is shown in figure 1(a). Its distribution shows the mean particle size to be 0.1 to 3.4 ㎛. Graphite powder provided by Sigma-Aldrich is examined, and its mean particle size is found to be 2.8 to 7.7 ㎛, as shown figure 1 (b).

Table 1: Chemical composition of the Mn dust

Mn dust	Mn	Al_2O_3	CaO	SiO_2	MgO	C	S	P	Fe
Mass %	66.83	1.16	1.12	0.85	0.09	0.13	0.010	0.047	3.76



(a) (b)

Figure 1: Particle size distribution: (a) Mn oxide powder (b) Graphite powder

2.2. Mix order

The required carbon to reducc Mn oxide powder is calculated by the stoichiometric relationship as shown by the equation (1).

$$Mn_3O_4 + C = 3Mn + 4CO \quad (1)$$

In order to examine the effect of carbon content on degree of reduction, mix orders are prepared with two carbon ratios in the mixture of raw materials; 100 and 130% required carbon as determined by the equation (1).

2.3. Composite pellet

Mn oxide and graphite powders are weighed to get the predetermine amounts calculated by the equation (1) and mixed thoroughly without binder. The mixture is pressed into pellet of 21 mm dia. and 16 mmH. These are stored in a desiccator.

2.4. Experimental procedure

Prior to experiment, the pellet and an alumina crucible are weighed, and the pellet is placed in the alumina crucible. The sample-alumina crucible assembly is positioned in a uniform temperature zone of a horizontal resistance furnace. After closing both ends of furnace tube, Ar gas is introduced at the flow rate of 1l/min. After a sufficient time to purge the furnace, the furnace is heated at rate of 10°C/min. until temperature reaches to 500°C. Thereafter, the furnace temperature is raised at the rate of 2 to 3°C/min. up to predetermined temperature. After reaction for 1 hour at this temperature, the sample-alumina assembly is cooled under a continuing Ar gas flow in the furnace. At room temperature, the sample-alumina assembly is withdrawn from the furnace and weighed to measure the weight loss. Figure 2 shows the arrangement of sample in the resistance furnace. In order to examine the effect of temperature the above experimental procedure is carry out at 1150, 1200,

1250, 1300, 1350, 1375, 1400, and 1450°C with the mix order of 100% required C. With the mix order of 130% required C, the experiment is carried out at 1300, 1350, and 1375°C. The sample-crucible assembly after the reaction is examined visually. Samples are collected for chemical and X-ray diffraction analyses.

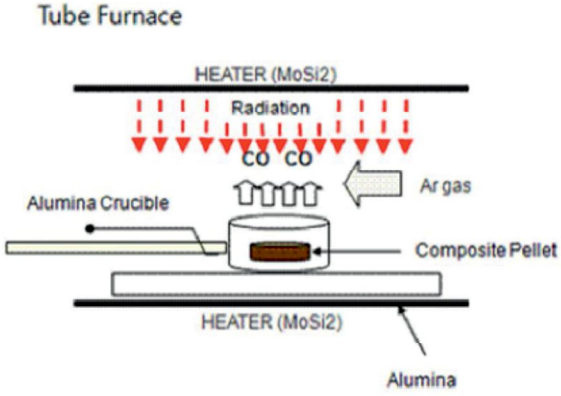


Figure 2: Arrangement of sample in furnace

3. RESULTS

3.1. Behavior of composite pellets at various reaction temperatures

Visual examination of reacted pellet shows that the appearance and shape are changed as the reaction temperature increase. Figure 3 shows this variation of reacted samples with mix order of 100% required C. All reacted pellets have a grayish appearance. The cylindrical shape and integrity of pellets are maintained as temperature increased from 1150 to 1250°C, although it gradually shrinks. However, the shape and integrity of pellets begin to break apart at 1300°C, and metallic appearance begins to dominate as temperature increases further with some residual MnO. This feature is shown in figure 4. It appears that Mn alloy begins to form at about 1300°C, and some residual MnO is observed because that mix order is carbon deficient.

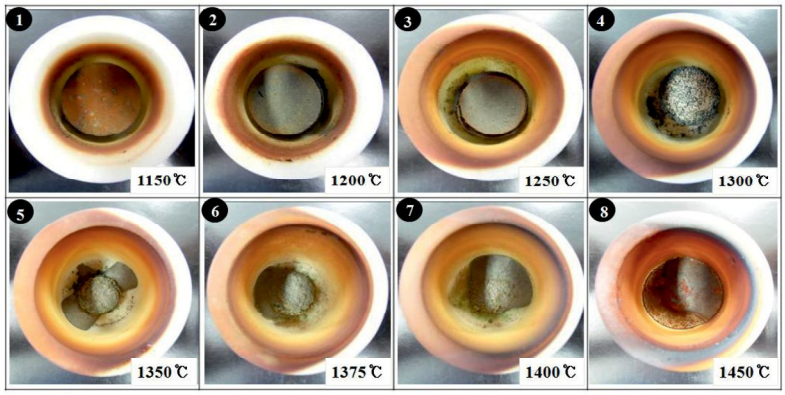


Figure 3: Shape and appearance of pellet at various temperatures with mix order of 100% required C

3.2. Degree of Reduction

The observed weight loss of pellet is the consequence of CO formation. Therefore, the degree of reduction is defined by the lost oxygen as CO to oxygen in raw pellet as given by the equation (2).

$$\text{degree of reduction}(\%) = O_{co} / O_i \times 100 \quad (2)$$

where, O_{co} is oxygen lost as CO and O_i oxygen in raw pellet.

The observed weight loss and degree of reduction are presented in table 2.

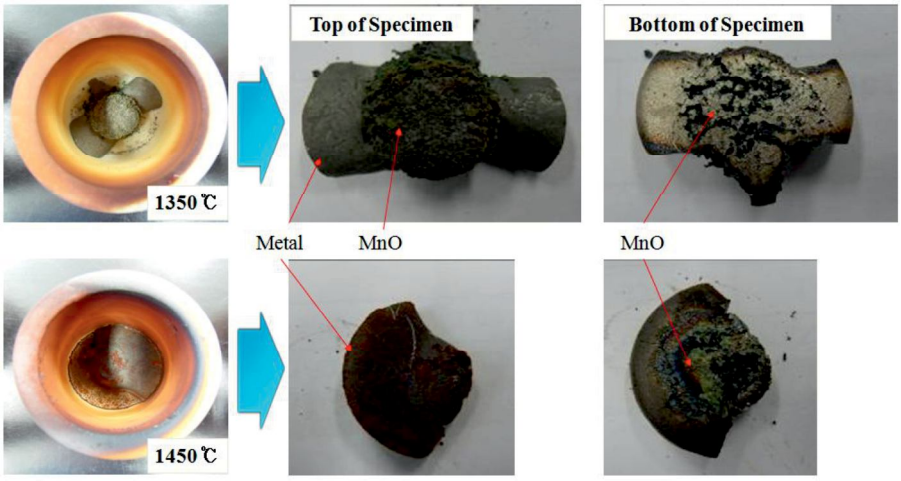


Figure 4: Mn alloy with residual MnO

Table 2: Weight loss and degree of reduction

	Temp.,℃	Initial Pellet weight, g	Weight Lost, g	degree of reduction, %
100% required Carbon	1150	17.95	2.32	34.33
	1200	17.98	3.18	47.10
	1250	17.96	4.59	67.96
	1300	17.98	5.97	88.28
	1350	18.00	6.20	91.67
	1375	17.96	6.00	88.85
	1400	18.00	6.20	91.67
	1450	17.97	6.44	95.47
130% required Carbon	1300	18.16	5.83	96.18
	1350	17.93	6.23	102.89
	1375	18.05	6.28	103.74

Figure 5 shows the variation of degree of reduction with reaction temperatures. The degree of reduction is shown to increase linearly with temperature as it increases 1150 to 1300°C. It is same at 1300°C for both mix orders of 100 and 130 % required C. At higher temperatures, degree of reduction increases slowly with temperatures, although it at 130 % required C is higher than that at 100% required C. When this observation is compared with the appearance of Mn alloy at 1300 °C as shown in figure 3, the smelting reaction to form Mn alloy appears to begin at about 1300°C.

Mn alloys are analyzed for Mn and C. Table 3 shows the analysis. Mn alloys produced with mix order of 100% required C contain C at 4.67 % on average while those with 130 % at 9.9 % on average. The phase diagram of Mn-C system indicates that C content in Mn is in the range of 7.3 to 7.7wt. % at 1300 to 1450°C in saturation with graphite. It indicates that the mix order of pellets is carbon deficient with 100 % required C.

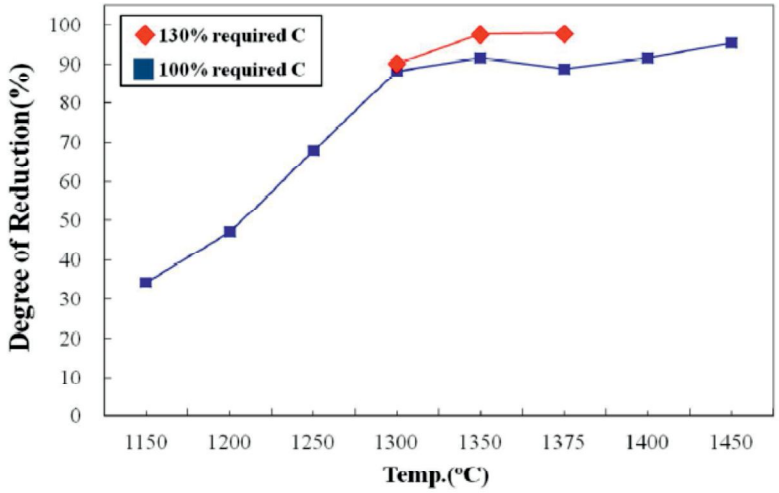


Figure 5: Degree of reduction at various temperatures

Table 3: Chemical analysis of Mn alloy

	Temp., °C	Analysis	
		Mn, wt.%	C, wt.%
100% required Carbon	1350	88.26	5.14
	1375	88.66	4.42
	1400	88.77	4.87
	1450	88.31	4.23
	Average	**88.50**	**4.67**
130% required Carbon	1300	75.97	10.57
	1350	77.14	10.27
	1375	78.99	8.86
	Average	**77.37**	**9.90**

3.3. XRD Analysis

The results of XRD analysis are shown in figure 6 with mix order of 100 % required C and in figure 7 with that of 130 %. With mix order of 100 % required C, samples are observed to consist of MnO, Mn_7C_3, and graphite at 1150 to 1250°C, figure 6 (a), and of Mn, MnO, and $Mn_{23}C_6$ at 1300 to 1450°C, figure 6 (b). It is noticeable that Mn_3O_4 is not observed at temperatures higher than 1150°C and no graphite at 1300 to 1450°C. This indicates that MnO, not Mn_3O_4, participates in Mn alloy smelting reactions and that the mix order with 100 % required C is carbon deficient.

Figure 7 shows XRD results with mix order of 130 % required C at 1300 to 1375°C. Mn alloys are observed with Mn_5C_2, Mn_7C_3, and graphite. The presence of graphite indicates that the mix order with 130 % required C supplies carbon in excess.

4. DISSCUSION

Mn_3O_4 is reduced to MnO at temperatures lower than 1150°C. Figure 5 indicates that this conversion may take place at 1050°C. This experiment evidence shows that MnO, not Mn_3O_4, participates in carbothermic reduction at temperatures higher than 1150 °C.

The carbothermic reducing reactions of Mn oxide powder is observed to take place in two

different modes as temperature increases beyond 1150°C; (1) formation of the Mn carbide (Mn_7C_3) at temperatures less than about 1300°C and (2) formation of Mn alloy at higher than that. The reaction mechanisms are discussed by analyzing and interpreting the experimental evidences from the present study. The present interpretation is supplemented by the information of the phase diagram for Mn-C system.

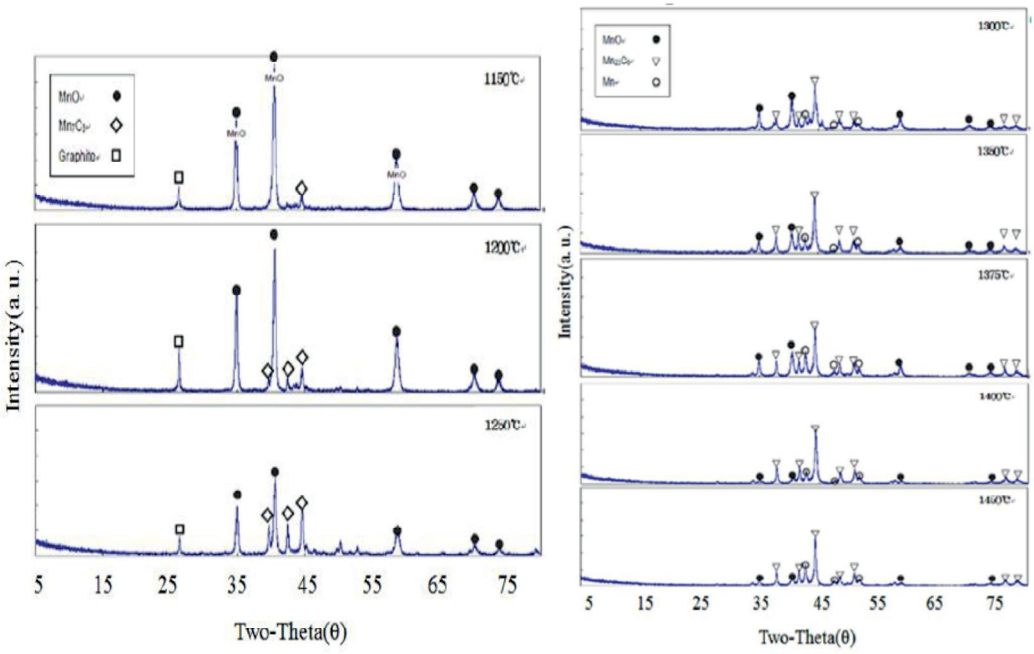


Figure 6: XRD analysis with 100% required carbon (a)1150 to 1250°C and (b) 1300 to 1450°C

The phase diagrams for Mn-C system are reported by Massalski [2] and Fenstad [3]. Both information do not agree on peritetic temperature, 1350°C by Massalski and 1328°C by Fenstad. Their phase diagrams are reproduced together in figure 8. This suggests that some uncertainty is involved in the information of peritectic reaction. But it is apparent that the peritectic reaction involving Mn_7C_3 is around 1300°C.

The phase diagram by figure 8 shows that five Mn carbides ($Mn_{23}C_6$, $Mn_{15}C_4$, Mn_3C, Mn_5C_2, and Mn_7C_3) are reported to form in the Mn-C system at temperatures less than about 1300°C. A noticeable feature in relevance to the present analysis is that Mn_7C_3 is stable at temperatures less than around 1300°C and dissociates into Mn alloy melt and graphite through a peritectic reaction at 1300°C and higher temperatures.

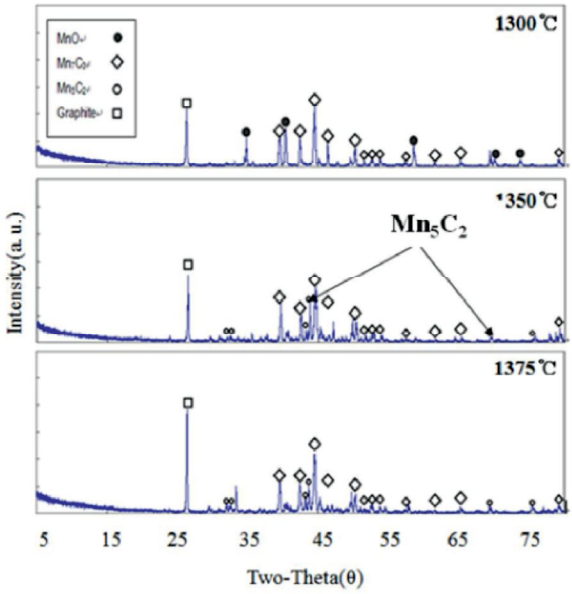


Figure 7: XRD analysis with 130 % required carbon at 1300 to 1375°C

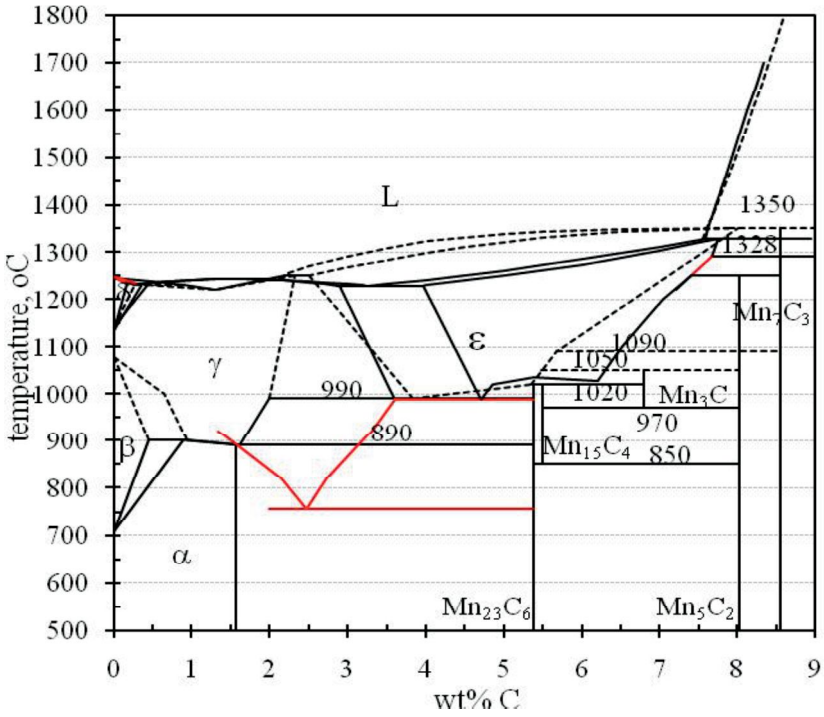


Figure 8: Mn-C phase diagram

4.1. Formation Mn_7C_3 from MnO at temperatures less than 1300℃

Mn_3O_4 (Hausmnnite) ins the raw materials is completely reduced to MnO (Manganosite) at about 1050 °C. With further increase of temperature, MnO is observed to be reduced to form Mn_7C_3 as represented by equation (3).

$$MnO + C \rightarrow Mn_7C_3 + CO \quad (3)$$

This reaction takes place in a solid state, and the reacted pellet is observed to maintain its mechanical integrity although its volume experiences some degree of shrinkage due to the loss of C and O mass.

The degree of Mn_7C_3 formation continues to increase with increasing temperatures up to about 1300°C, and its increasing rate with temperature is same for both carbon ratios in the mix order, 100 and 130 % required C. The formation of four lower forms of carbide ($Mn_{23}C_6$, $Mn_{15}C_4$, Mn_3C, and Mn_5C_2) is not detected. The reason of it is not clear at present, but it is suggested that the intimate presence of graphite particles at reaction sites is able to maintain the driving force of carbon high and that the reaction time of one hour is sufficient enough to transform all lower carbides to the highest carbide, Mn_7C_3, at all investigated temperatures.

It also indicates that the reduction of MnO is complete only when a sufficient amount of carbon is available for the conversion of remaining MnO after satisfying the formation of Mn_7C_3. Taking into account of Mn_7C_3 formation, the stoichiometric relationship of this reducing reaction is described by the equation (4).

$$7MnO + 10C = Mn_7C_3 + 7CO \quad (4)$$

The chemical and XRD analyses of Mn alloys after the experiment show that the mix orders are evidently deficient in carbon when they are prepared at 100 % required C by equation (1). On the other hand, the experimental results with mix orders at 130 % required C do not show a trace of MnO, and the analysis of Mn alloys is observed to be 9.9 %C on average. This indicates that the mix order with 130 % required C does provide sufficient enough carbon to reduce MnO completely. The above consideration suggests that Mn_7C_3 is the intermediate product in the carbothermic reduction of Mn oxide powder and that its formation precedes the production of Mn alloys.

4.2. Formation of Mn alloys at temperatures higher than about 1300°C

Mn alloy are observed to form at temperature about 1300°C and higher. As it is not stable at these temperatures, Mn_7C_3 formed at lower temperatures decomposes into Mn alloy and graphite. Mn alloy at these temperatures is present as melt and dissolves carbon in it. Therefore, the reduction of MnO at temperatures higher than about 1300°C takes places by carbon as described by the equation (5).

$$MnO + C = Mn + CO \quad (5)$$

Because of its fluid nature, Mn alloy is separated out from a remnant MnO from the reaction forming Mn_7C_3. MnO is observed only when the mix order is deficient in carbon.

The XRD analysis shows that Mn alloys are found to contain $Mn_{23}C_6$ when the mix orders are deficient in carbon and Mn_7C_3, Mn_5C_3, and graphite when they are sufficient in it. As discussed above, Mn carbides are not stable at temperatures higher than about 1300°C. Therefore, the observed Mn carbides in smelted Mn alloys are originated from the precipitation during cooling.

5. CONCLUSION

In the carbothermic reduction of Mn oxides, Mn_3O_4 is reduced to MnO at temperatures lower than 1050°C. Thereafter, MnO reacts with carbon to form Mn_7C_3 until temperature reaches to about 1300°C. According to the available phase diagram of Mn-C, Mn_7C_3 is not stable and dissociates into Mn alloy and graphite through peritectic reaction at about 1300°C and higher. As temperature

increases higher than about 1300°C, therefore, the reduction of MnO is taken place by the dissolved carbon in Mn alloy.

6. ACKNOWLEDGEMENT

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