Practical reduction of manganese oxide.

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Accepted on August 16, 2017

Editorial

Manganese is an important metal used in steel industry. It is abundant in steel as an alloying element. Additionally, it is used as a deoxidiser in steel production. In steel industry, manganese metal is used as an intermediate product of ferromanganese. Ferromanganese is generally produced by reduction of oxidised manganese. Reduction is in the form of either metalothermic reduction or carbothermic reduction. Practically, metallographic reduction is performed with silicon or aluminium which form more stable oxides than magnesium. Carbothermic reduction means reduction with carbon. All of the reduction reactions are highly endothermic and a high amount of thermal energy is required for the accomplishment of these reactions [1, 2]. The most abundant forms of the manganese oxides are MnO_2, Mn_2O_3, Mn_3O_4 and MnO. These compounds dissociate during heating.

$2MnO_2 = Mn_2O_3 + 1/2O_2$

$3Mn_2O_3 = 2Mn_3O_4 + 1/2O_2$

$Mn_3O_4 = 3MnO + 1/2O_2$

Therefore, different oxide phases are formed dependent on the temperature and partial oxygen pressure. Mn-O-C system is given in Figure 1 in different partial oxygen pressures and different temperatures for $\frac{m^{Mn}}{m^{c}} = 1$.

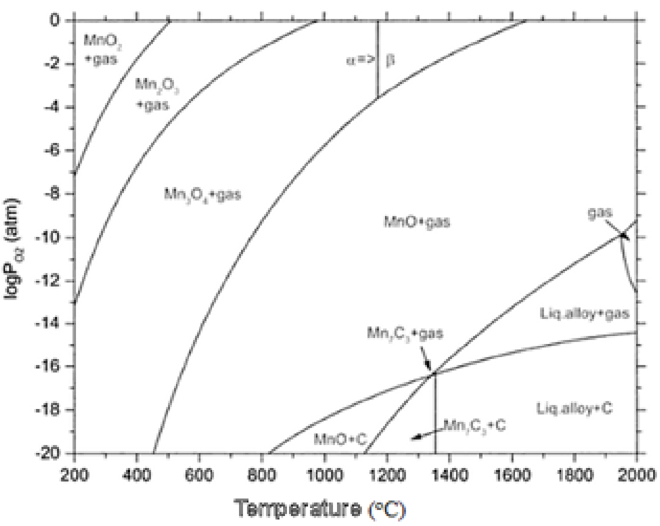

Figure 1. *Mn-O-C system in different partial oxygen pressures and different temperatures* ($\frac{m^{Mn}}{m^{c}} = 1$)[3].

Reduction of manganese oxides is considered in two steps. The first step is the reduction of oxygen-rich oxides to MnO and the second one is the reduction of Mn to metallic manganese. Reduction starts with the transformation of MnO_2 into Mn_2O_3 and Mn_2O_3 into Mn_3O_4 at temperatures over 450°C, then these two phases are reduced by either carbon or carbon monoxide in the system of Mn-C-O. The reduction reactions of manganese oxides and the standard free energies of formation of these chemical reactions are given in Table 1 [3-8].

A very high carbon monoxide pressure is required for the reduction of MnO with carbon monoxide. Change of ratio of partial equilibrium pressures of carbon monoxide and carbon dioxide with temperature is presented in a diagram given in Figure 2 related to the reduction reaction of MnO with carbon monoxide and Boudouard reaction [3].

As understood from the diagram, the reduction of MnO with carbon monoxide can only be achieved at temperatures over 1430°C at which the ratio P_CO/P_([CO]_2) is 7400. Since the reduction, if done with carbon monoxide, can only be achieved in the abundance of carbon, at temperatures over 1430°C and at an extremely high carbon monoxide pressure, the reduction of MnO with carbon monoxide can not be accomplished in many industrial applications. For this reason, reduction of MnO with solid carbon or iron carbide, as given in Table 1, comes forward [3-9]. Furthermore, manganese carbides are also formed

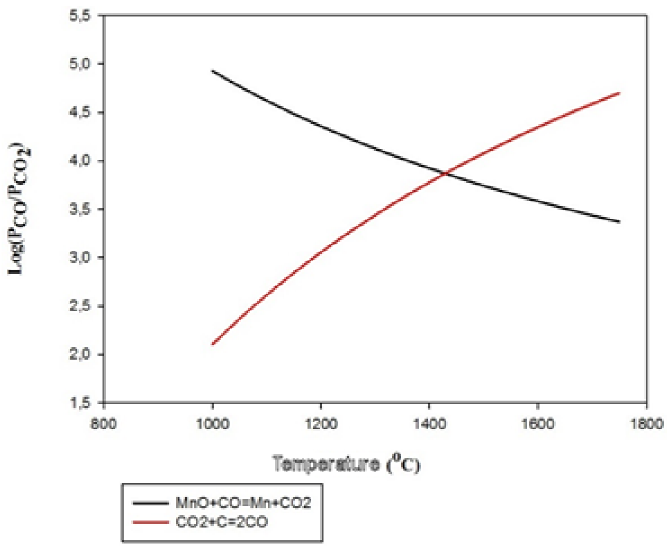

Figure 2. *Change of ratio of partial equilibrium pressures of carbon monoxide and carbon dioxide with temperature related to the reduction reaction of MnO with carbon monoxide and Boudouard reaction.*

Table 1. Reduction reactions of manganese oxides in different types and the standard free energies of formation of these chemical reactions in different temperature ranges.

Reactions	ΔG°. kJ/mol	T (°C)
Reduction reactions of oxygen-rich oxides to MnO		
$3Mn_2O_3 + C = 2Mn_3O_4 + CO$	ΔG° = - 0.25 – 0.17T	25-1100
$3Mn_2O_3 + CO = 2Mn_3O_4 + CO_2$	ΔG° = -170.71 – 0.004T	25-1100
$Mn_3O_4 + C = 3MnO + CO$	ΔG° = 110.96 – 0.21T	25-1244
	ΔG° = 84.35 – 0.20T	1244-1700
$M_3O_4 + CO = 3MnO + CO_2$	ΔG° = 110.96 – 0.21T	25-1244
	ΔG° = 84.35 – 0.20T	1244-1700
Reduction reaction of MnO with carbon monoxide		
$MnO + CO = Mn + CO_2$	ΔG° = 102.38 + 0.01T	25-1227
	ΔG° = 116.73 + 0.01T	1227-1727
Boudouard reaction		
$CO_2 + C = 2CO$	ΔG° = 170.82 – 0.18T	25-1727
Reduction reactions of MnO with carbon or iron carbide		
$MnO + C = Mn + CO$	ΔG° = 287.6 – 0.16T	25-1227
$MnO + 10/7C = 1/7Mn_7C_3 + CO$	ΔG° = 284.22 – 0.18T	717-1087
	ΔG° = 282.01 – 0.18T	1087-1137
	ΔG° = 280.22 – 0.18T	1137-1244
	ΔG° = 280.35– 0.18T	1244-1700
$MnO + 10/7Fe_3C = 1/7Mn_7C_3 + 30/7Fe + CO$	ΔG° = 246.09 – 0.15T	717-840
	ΔG° = 269.42 – 0.17T	840-1087
	ΔG° = 267.42 – 0.17T	1087-1137
	ΔG° = 265.42 – 0.17T	1137-1244

during the carbothermic reduction of manganese oxides. The temperature required for manganese carbide formation (1280°C) is lower than that required for metallic manganese formation (1430°C). Therefore, formation of metallic manganese is inevitable.

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