

Discussion: Reactions in the production of high-carbon ferromanganese from Mamatwan Ore*

by A. Koursaris and J. B. See

W. J. RANKIN†

The above paper is an important contribution to the field of physicochemical studies in ferromanganese production. The authors are to be congratulated on the well-planned and competently executed experimental work and on the interpretation of the data.

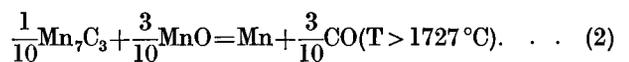
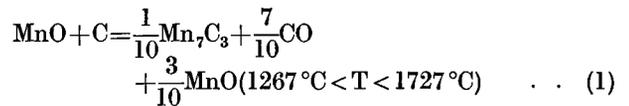
Although the paper is essentially descriptive, the results lend themselves to thermodynamic interpretation (but in such a complex system as that studied this cannot be done rigorously), as well as to an examination of the probable reduction mechanisms that operate at various stages. The authors attempt this, but because I feel they have not dealt fully with these aspects, I offer the following discussion.

Thermodynamics of Reduction of Manganese Ores by Carbon

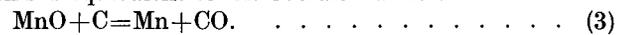
This is best examined in terms of the Pourbaix diagram for the Mn-O-C system shown in Fig. 1, which was constructed by Downing¹ from the available thermodynamic data for manganese oxides and carbides. The line AB in Fig. 1 shows the reduction sequence of manganese oxides in the presence of carbon for a total pressure of 1 atm. The higher oxides of manganese (Mn₂O₃

and Mn₃O₄) are unstable at all temperatures in the presence of carbon and react to form MnO. Manganous oxide itself is stable up to about 1267°C, above which temperature it reacts with carbon to form the manganese carbide Mn₇C₃. Depending on the initial carbon-to-MnO ratio, some MnO may remain after all the carbon has reacted. If this is the case, a further reaction occurs above about 1727°C in which the Mn₇C₃ and MnO react to form manganese metal. Again depending on the initial carbon-to-MnO ratio, some Mn₇C₃ may remain when all the MnO has reacted. If the initial carbon-to-MnO ratio were such that no MnO remained after Mn₇C₃ had formed, the final reduction product would be Mn₇C₃ and no metallic manganese would form.

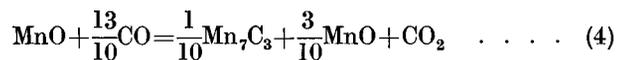
If pure manganese metal is the desired final product, it is necessary to start with a carbon-to-MnO ratio of 1. Then the reaction sequence on heating a mixture from room temperature is



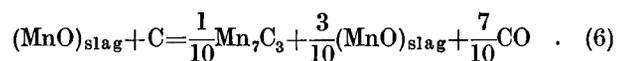
This is equivalent to the overall reaction



Reactions (1), (2), and (3) do not necessarily indicate the reaction mechanism, merely the stoichiometric relation between the reactants and the products. Reaction (1), for example, involves no slag phase in the pure Mn-O-C system, and occurs almost certainly by interaction of solids and gas rather than by interaction of two solids as written. The equations representing the mechanism of reaction (1) are



which when summed are stoichiometrically the same as reaction (1). It is a consequence of Hess's law that, if reaction (1) occurs at a total pressure of 1 atm between 1267 and 1727°C, then so can reactions (4) and (5) since the state of the reactants and products is the same. The reason for postulating reactions (4) and (5) as the reaction mechanism is the much more rapid reaction that is possible between a gas and a solid than between two solids. Alternatively, in the presence of slag containing MnO, reaction (1) could then occur by interaction between a solid and a liquid:



In work recently conducted by the writer², equimolar mixtures of MnO and graphite were heated under argon at temperatures in the range 1200 to 1425°C. The phases present after reaction were identified by X-ray diffraction as MnO and Mn₅C₂, and not Mn₇C₃ as predicted by

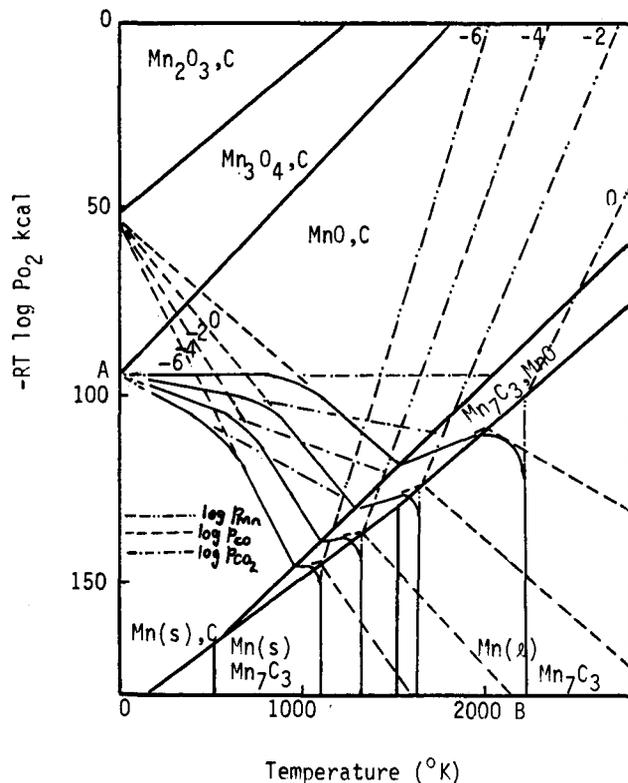


Fig. 1—Pourbaix diagram for the Mn-O-C system¹

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†University of Stellenbosch, Cape Province.

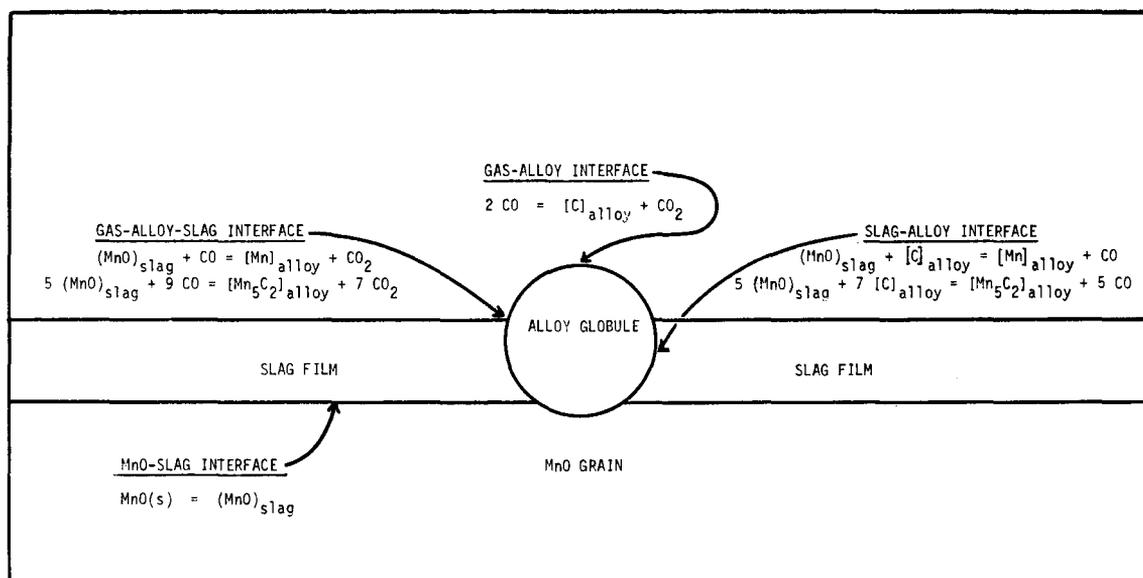


Fig. 2—Mechanism of reduction of MnO in second stage of reduction by carbon

Downing's calculation. This, however, does not invalidate the Pourbaix diagram shown in Fig. 1, and the stability region for Mn_5C_2 is absent only because of the lack of knowledge of its standard free energy of formation. Mn_5C_2 is stoichiometrically not very much different from Mn_7C_3 , and their standard free energies of formation should be of the same order. As a rough approximation, one can replace Mn_7C_3 by Mn_5C_2 in the appropriate stability fields in Fig. 1.

If FeO is also present with MnO , one would expect it to be reduced to iron before the reduction of MnO since it is much less thermodynamically stable, and this was found to be the case by Koursaris and See. The presence of metallic iron may, however, affect the subsequent reduction of MnO for two reasons.

- (1) It allows reaction (3) to occur at very much lower temperatures by avoiding the necessity to form metallic manganese at unit activity. Manganese and iron are mutually soluble, and manganese may alloy with iron at a lower activity than unity. This is illustrated by the following calculations:

$$K_3 = \frac{a_{\text{Mn}} p_{\text{CO}}}{a_{\text{MnO}} a_{\text{C}}}$$

$= a_{\text{Mn}}$ (at a pressure of CO of 1 atm and in the presence of pure MnO and C).

Based on Coughlin's³ free energy data for MnO and CO , the activity of manganese at 1227°C is 0,09 and at 1327°C is 0,37. Iron and manganese form an ideal solution, and, because their atomic masses are 56 and 55 respectively, the equilibrium concentration of manganese in the iron is 9 and 37 mass per cent at 1227 and 1327°C respectively. Koursaris and See report manganese contents of the alloy from 10 per cent at 1300°C to over 80 per cent at 1600°C , and this tends to confirm that reaction (3) occurs in practice.

- (2) It is possible, though this is much less certain, that a mixed iron-manganese carbide forms at tempera-

tures below that required for the formation of pure Mn_5C_2 . Without thermodynamic data for a mixed carbide, it is not possible to predict whether such a phase would form, nor do the data of Koursaris and See provide much information because of the difficulty in distinguishing X-ray diffraction peaks of the possible carbides.

Mechanism of Reduction of Manganese Ores

Koursaris and See identify three stages in the reduction of the ore, and it is interesting to speculate further on the possible mechanisms of reduction that operate in each stage.

In the first stage, calcite and dolomite decompose at temperatures between 600 and 900°C , making the ore porous and permitting reduction of the higher oxides of manganese and of the iron oxide by carbon monoxide. This results in the formation of coarse grains of MnO , a primary calcium silicate slag, which forms a film on the surface of the particles and a continuous network in the interior, and metallic iron, which is present as small globules throughout the grain as well as on the surface.

As the slag film develops, penetration of carbon monoxide into the particles is stopped, and the second stage starts with the slow dissolution of the MnO grains in the primary slag. This provides a mechanism by which MnO may diffuse rapidly to the surface and hence to the slag-metal interface between the iron globules on the surface and the slag film. Reduction to metal by carbon may then occur in two possible ways:

- (1) by carbon monoxide at the slag-metal-gas three-phase interface
- (2) by carbon dissolved in the alloy by exposure to the carbon monoxide atmosphere.

The reactions that probably occur at this stage are illustrated in Fig. 2. By this mechanism, the surface globules continue to grow in size as reduction occurs, while the globules within the grains remain at a constant size.

The third and final stage occurs as the volume of slag

increases, and good contact between it and the lumps of solid reductant is achieved. At this stage direct reduction of manganese from the slag by the solid reductant occurs to a significant extent for the first time, and probably becomes the predominant reaction mechanism at the stage where metal is no longer in direct contact with the gas phase but is isolated from it by the slag.

Authors' reply

Rankin's application of theoretical considerations to elucidate the reactions and mechanisms involved in the reduction of Mamatwan manganese ore is greatly appreciated, but they require some qualification.

Rankin considers that the thermodynamics of reduction of manganese ores can best be examined in terms of the Pourbaix-Ellingham diagram for the Mn-O-C system.

Downing's diagram pertains to a system containing only manganese, oxygen, and carbon. Downing established the phase boundaries in the diagram by assuming that there is no solubility between the condensed phases. The diagram gives an accurate indication of the boundaries between the different pure manganese oxides, and possibly between MnO and the first metallic species to form (presumably Mn_7C_3), since extensive solubility between Mn_7C_3 and MnO is not expected.

In the paper under consideration, the discussion on the reduction of the higher oxides of manganese to MnO was confined to simple statements because the investigation aimed primarily at a study of the processes in the hotter regions of submerged-arc furnaces. Furthermore, the reduction of the higher oxides to manganous oxide has been dealt with extensively in the literature, and the reduction of the manganese compounds in Mamatwan ore has been investigated by Grimsley and Pentz.

In Mamatwan ore, the manganese occurs mainly as braunite ($3Mn_2O_3 \cdot MnSiO_3$), which is more stable than pure Mn_2O_3 , and experimental evidence¹ shows that at no stage during the process do any of the manganese oxides occur as a pure oxide. The impurities in the different oxides, which are SiO_2 , FeO, MgO, and CaO, stabilize the manganese oxides, and the phase boundaries in the Pourbaix-Ellingham diagram would be shifted by unknown amounts from their 'ideal positions'.

Downing established the boundary between the MnO-C and MnO- Mn_7C_3 fields by exploiting the following equilibria:



$$\Delta G^0_1 = 190,8 - 0,047T \text{ kcal (1500 to 2050K)} \quad \text{(ref.2)}$$



$$\Delta G^0_2 = -4,51 - 0,0047T \text{ kcal (1517 to 1973K)} \quad \text{(ref.3)}$$



$$\Delta G^0_3 = 186,29 - 0,0447T \text{ kcal.}$$

The equilibrium constant, K_3 , for reaction (3) was taken to be

$$K_3 = P_{O_2}$$

by the assumption of unit activity for the condensed phases.

References

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3. COUGHLIN, J. P. Contributions to the data on theoretical metallurgy. XII. Heats and free energies of formation of inorganic oxides. U.S. Bureau of Mines, *Bulletin no. 542*, 1954.

Then,

$$\Delta G^0_3 = RT \ln K_3 = -RT \ln P_{O_2}.$$

Simple calculation shows that the vertical axis of Downing's original diagram and Rankin's reproduction of it should be labelled $-RT \ln P_{O_2}$ and not $-RT \log P_{O_2}$. Equilibria along similar lines can be written to establish the boundary between the Mn_7C_3 -MnO and Mn_7C_3 -Mn fields.

Downing used the data for Mn_7C_3 given by Elliott³, who points out that 'only data from 1075°K to 1235°K may be considered to be reasonably accurate'. There is therefore reasonable uncertainty with regard to the position and extent of the Mn_7C_3 -MnO field. Downing's diagram depicts two phases above 1727°C, namely liquid manganese and Mn_7C_3 . That these phases exist as such at these temperatures is not at all certain. This imposes serious uncertainties with regard to the position of the boundary between the Mn_7C_3 -MnO and Mn- Mn_7C_3 fields since the boundary was determined on the assumption that there is no solubility between the condensed phases. What probably exists at these temperatures is a liquid solution of carbon in manganese.

It is therefore evident that the Pourbaix-Ellingham diagram has limitations even when the ideal system is considered. The application of this diagram to the system under discussion may give incorrect results as will be seen presently.

In his discussion, Rankin considers that reaction (3) is the overall reaction for reactions (1) and (2). It is very doubtful that this is the case since reactions (1) and (2) occur in different temperature ranges. Reaction (3) may be the overall reaction at temperatures greater than 1727°C. However, Rankin uses reaction (3) to predict the equilibrium manganese content of the alloy at 1300°C. Furthermore, Rankin does not take into account the fact that the alloy contained carbon, which causes a negative deviation⁴ from Raoult's law for manganese. That Rankin obtained a theoretical manganese content very close to the actual is purely fortuitous. Proof of this is the fact that Grimsley obtained over 80 per cent reduction of precalcined Mamatwan ore at 1300°C. The precise manganese content in Grimsley's alloys is not known, but it can be estimated at about 80 per cent. The amount of manganese in the alloy formed at 1300°C under SCICE conditions was not a result of thermodynamic, but of kinetic, limitations. Here it is not suggested that reaction (3) as proposed by Rankin does not occur.

Rankin considers that the formation of a mixed iron-manganese carbide is not very likely at temperatures

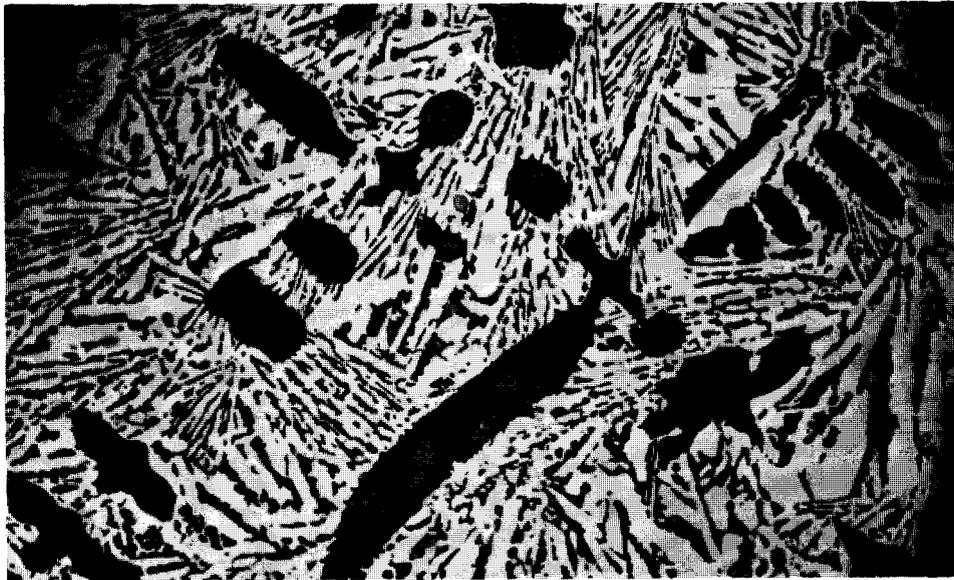


Fig. 1—The structure of a globule of alloy that formed when ore and coke were heated to 1300°C at 350°C per hour and then cooled. Primary austenite appears as dark dendrites. The matrix consists of a eutectic of austenite and a mixed iron-manganese carbide (bright). Etched, 2 per cent HNO₃ in alcohol, X50.

below that required to form Mn₅C₂. It is now certain that a mixed carbide forms, although the precise temperature at which it forms is not known. Fig. 1 shows the structure of a globule of alloy from a charge of ore and coke that was heated to 1300°C and cooled. The alloy consists of primary dendrites of austenite in a eutectic of austenite and mixed iron-manganese carbide. From the structure of the globule, it is clear that the alloy was liquid at 1300°C, i.e. it was a mixture of manganese, carbon, and iron. The overall manganese content of the globule was about 10 per cent. The carbon content was estimated at about 4 per cent. The phases were studied by X-ray-diffraction analysis, microhardness tests, and microprobe analyses. The mixed carbide persisted under all experimental conditions, while the primary austenite vanished above 1400°C. Small amounts of a second constituent, which was not precisely identified, were present in alloys formed at 1600°C. It is believed that the mixed carbide can be formed at temperatures as low as 1150°C.

It is clear from the above considerations that reactions (1) to (3), and consequently the Pourbaix-Ellingham diagram, have little to offer in aiding the interpretation of the processes that occur during the reduction of Mamatwan ore.

According to Rankin, the mechanism of reaction is represented by reactions (4) and (5) because reaction between a gas and a solid is much faster than between two solids. This is acknowledged. However, in the case

under discussion there is no basis for comparison. The effectiveness of carbon monoxide as a reducing agent cannot be determined since it co-existed with free carbon and carbon dissolved in the alloy.

Research⁵ on the reduction of iron oxides by carbon showed that the rate of reduction increases with increasing reactivity of the carbon towards carbon dioxide. Grimsley's results and those of the investigation under discussion suggest that the reactivity of the carbon has little or no influence on the rate of reduction of the MnO produced during the reaction of Mamatwan ore.

Rankin's Fig. 2 is accepted, although reservations must be expressed on two counts.

- (a) The effectiveness of carbon monoxide as a reducing agent for MnO is not known.
- (b) It is not certain that the mechanism of reduction can be expressed by chemical equations that depict the formation of a carbide as an entity.

References

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