

# Thermodynamics of Iron-Manganese Aluminate Spinel Inclusions in Steel

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The effect of manganese on the residual oxygen concentrations of liquid iron in equilibrium with alumina saturated iron-manganese aluminate spinel solid solutions was investigated at temperatures of 1550, 1600, and 1650°C. The relationship between the equilibrium concentrations of manganese and oxygen in iron melts containing up to 6 wt pct manganese has been established. The compositions of the spinel deoxidation products,  $(\text{Fe}_x\text{Mn}_{1-x})\text{O} \cdot \text{Al}_2\text{O}_3$ , which were formed during equilibration with the iron melts were determined with electron microprobe and neutron activation analysis. From these results, new thermodynamic data pertaining to galaxite formation reactions have been derived and their implications with respect to the deoxidation of aluminum semikilled, silicon free, steels have been discussed.

**I**N aluminum killed steel, oxide morphology is generally well controlled. Sulfides, however, are plastic during hot rolling and form stringer inclusions which adversely affect formability and transverse toughness properties. This is particularly the case in high strength low alloy grades and for this reason sulfide modifiers such as zirconium or rare earths are generally added. Increasing attention is now being given to the production of aluminum semikilled steels in which the oxygen content is sufficiently high to ensure the formation of relatively nonplastic oxysulfides. This obviates the need for sulfide shape control agents. At the same time, the silicon level is minimized in order to avoid the formation of silicate stringers. Under these conditions, in the presence of manganese or chromium the main oxide inclusions should consist of solid solutions of iron-manganese aluminate spinels or iron aluminochromite spinels, which are solid at steelmaking temperatures and retain their shape during hot rolling. In the presence of silicon, these compounds are generally found agglomerated together within a silicate matrix in the form of a massive defect.<sup>1</sup> In the absence of silicon, and thus silicates, there is a greater opportunity for any alumina or aluminate spinel solid solutions which remain in the steel after solidification to be more uniformly dispersed and hence constitute less of a problem.

While numerous investigations pertaining to deoxidation reactions involving the formation of alumina have been reported,<sup>2-9</sup> there have been fewer studies concerning the formation of hercynite<sup>10-15</sup> or galaxite,<sup>16-22</sup> during deoxidation of molten steel.

The primary objective of the present study was to establish accurate values for the manganese/oxygen content of molten iron in equilibrium with alumina and spinel solid solutions containing hercynite and galaxite, and to determine the thermodynamic conditions which govern the formation of these spinel compounds during deoxidation reactions. Experiments to determine the effects of up to 6 pct manganese on the residual oxygen concentration in iron melts and also on the composi-

tion of the deoxidation products, were conducted in the temperature range 1550 to 1650°C, in alumina crucibles contained within an induction furnace, under an argon atmosphere.

## EXPERIMENTAL ASPECTS

The pure iron, which served as a base material, was obtained in the form of 25 mm diam rods of Ferrovac-E.

A typical analysis is given in Table I. Crucibles and thermocouple sheaths were of high purity recrystallized alumina. Manganese dioxide, ferric oxide, and  $\alpha\text{-Al}_2\text{O}_3$  of chemical reagent grade were obtained in powder form. These materials together with powders of metallic iron (>99.99 pct) and manganese (>99.9 pct) were used for the preparation of synthetic spinels. The procedure is described elsewhere.<sup>23</sup> The manganese powder was also used for the preparation of ferromanganese alloys for additions to the iron melts.

### The Furnace Arrangement and Experimental Procedure

A schematic cross-section of the vertically mounted working tube, including the crucible assembly is shown in Fig. 1. The working tube, 44 mm ID and 610 mm long, was of high purity silica, fitted at the top and bottom with water cooled brass caps through 'O' ring seals. The top cap contained several openings for pressure measurement, temperature measurement, gas inlet, melt observation, melt additions, and sampling.

The silica working tube containing the crucible assembly was placed within an induction coil, powered at a constant frequency of 10,000 Hz by a Tocco motor generator driven by a 3 phase-550 V source. Cleaned Ferrovac-E rod, about 130 g in weight was placed in an alumina crucible, which was in turn positioned within an outer protective alumina crucible, and the space between the two, filled with alumina powder. Experiments were conducted with and without the addition of spinel solid solutions. When an addition was required approximately 0.5 g of the appropriate compound was compacted on the base of the reaction crucible. Prior to melting, the tip of the thermocouple sheath was positioned within a central hole in the iron ingot at a distance of approximately 4 mm above the base of the

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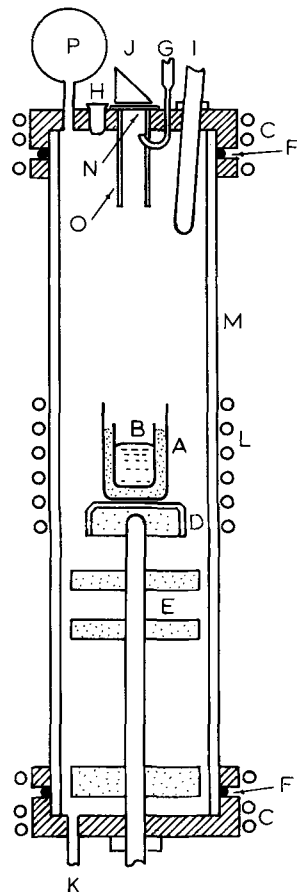


Fig. 1—The furnace assembly. A—alumina crucible, B—melt, C—water cooled cap, D—crucible support, E—radiation baffle, F—'O' ring seal, G—gas inlet, H—rubber stopper, I—thermocouple sheath, J—prism, K—gas outlet, L—induction coil, M—quartz tube, N—glass plate, O—fume baffle, P—pressure gage.

Table I. Typical Analysis for Ferrovac-E

Element	Wt Pct
C	0.004
P	0.001
S	0.006
Mn	0.001
Si	0.007
Cu	0.001
Cr	0.010
Sn	0.002
Ni	0.033
Mo	0.010
V	< 0.002
Al	0.010
Ti	0.002
B	0.0005
Cb	< 0.002
Co	0.003
Zr	0.002
H	0.0036
O	0.046
N	0.005

reaction crucible. Working temperatures between 1550 and 1650°C were measured with a platinum-rhodium thermocouple (Pt/5 pct Rh-Pt/20 pct Rh) the accuracy of which was checked against the melting point of pure iron in an atmosphere of hydrogen. These checks yielded values within ±2°C of the accepted melt-

ing point (1536°C). The actual experiments were conducted under closed conditions in which the pressure was maintained at approximately 1.1 atm. During an experiment suction samples were taken intermittently from the melt with a quartz tube.

#### Sample Preparation and Chemical Analysis

At the end of each experiment the reaction crucible was broken into small fragments. The inner surface of these fragments exhibited homogeneous colors which were characteristic of the particular constituents and compositions. In order to remove any metallic particles which had adhered to the crucible walls, the fragments were treated with 5 pct HCl-alcohol solution<sup>24</sup> for about 4 h at approximately 80°C. Fragments were then analyzed by electron microprobe and neutron activation. The accuracy of these analytical techniques was established by taking into account the results obtained with synthetic spinel solid solutions of various known composition, which had been prepared previously for use as calibration standards. Additional information pertaining to the composition and morphology of the oxide reaction products was obtained by scanning electron microscopy. From portions of crucible fragments, thin layers of deoxidation product were flaked off, ground into a fine powder, and used for X-ray diffraction analysis.

A thin section approximately 2 to 3 mm in thickness was cut from the top portion of each ingot and used for microscopic examination. The main body of the ingot was cut into three sections. The upper portion was saved for manganese analysis with a Spectro-Vac spectrometer. The reproducibility of these analytical values was found to be within ±3 pct of the measured values. The central portion was cut into several pieces and used for oxygen analysis by inert gas fusion. From analysis of standard samples, reproducibility was found to be ±2 and ±4 ppm for samples containing oxygen of less than 66 ppm and higher than 400 ppm, respectively. Drillings were taken from the lower portion of the ingot for manganese analysis by colorimetry.<sup>25</sup> The reproducibility of the analytical results was within ±0.001 pct manganese.

Suction samples, usually 10 to 12 mm in length, 3 mm in diam, and 5 to 7 g in weight were cleaned, and cut into several sections for manganese analysis by colorimetry or electron microprobe. The reproducibility of the microprobe analysis was found to be within ±3 pct of the measured values. Small sections were also used for oxygen analysis.

Several sections from ingots were analyzed for aluminum using the Spectro-Vac unit. Reproducibility based on a standard sample containing 100 ppm, was within ±3 pct.

#### Attainment of Equilibrium

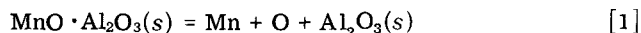
On equilibrating liquid iron-oxygen alloys containing various amounts of manganese with alumina, the reaction products formed are aluminate solid solutions ( $\text{Fe}_x\text{Mn}_{1-x}\text{O} \cdot \text{Al}_2\text{O}_3$ ), in which the value of  $x$  decreased from one to essentially zero as the amount of manganese in the alloy melt increased. As these changes occur, the amount of dissolved oxygen in the liquid alloys progressively decreases. In most experiments

equilibrium appeared to be attained within approximately two h. However, the experiments were generally continued for times ranging up to 8 h.

To ensure that the equilibrium values were accurate, it was desired that the final oxygen content of the melt be reached from both high and low initial oxygen levels. When a higher initial oxygen content was required, Fe<sub>2</sub>O<sub>3</sub> tablets were dropped into the melt immediately after the ingot was molten. The amount added was sufficient to supply a total starting oxygen content approximately 300 ppm above the equilibrium level. This excess oxygen reacted with the manganese in the melt and the alumina crucible wall to form a spinel solid solution of appropriate composition corresponding to the amount of manganese dissolved in the melt. On the other hand, when the initial oxygen content was lower than the equilibrium value, approximately 0.5 g of powdered aluminate spinel was compacted on the bottom of the reaction crucible. This material acted as an oxygen donor to the melt by partial dissociation.

### PRESENTATION OF RESULTS

The primary objective of this study was to establish the influence of manganese on the oxygen content of liquid iron in equilibrium with alumina saturated spinel compounds at temperatures in the range 1550 to 1650°C. The results obtained may be interpreted in terms of the following chemical reaction:



where the underlined symbols denote elements dissolved in liquid iron, and the subscript, (s) represents compounds present in the solid form. Experiments were designed to yield information pertaining to the following specific aspects:

- 1) Effect of manganese variations on the equilibrium oxygen content of the alloy melt.
- 2) Effect of manganese variations on the equilibrium composition of the spinel reaction product.
- 3) Effect of intermittent temperature variations on the equilibrium oxygen content.

#### Effect of Manganese Variations on the Equilibrium Oxygen Content of the Alloy Melt

The results obtained for the effect of manganese on the oxygen content of liquid iron in equilibrium with alumina and iron-manganese aluminate spinels at 1600°C are shown in Fig. 2. In this figure, the upper line shows the results for manganese concentrations up to 1 pct on an expanded scale, while the lower line shows all the results obtained over the full range of manganese contents investigated. All the results obtained at three temperatures, 1550, 1600, and 1650°C, are summarized in Fig. 3. In these figures the intercepts on the vertical axis at zero pct manganese correspond to the oxygen concentrations in liquid iron which had been equilibrated with alumina and hercynite. With increasing manganese concentrations, the equilibrium oxygen content rapidly decreases. For example, at 1600°C the equilibrium oxygen level falls from 740 to 165 ppm in the presence of 0.5 pct manganese. Above approximately 2.5 pct manganese, the oxygen content changes only slightly with further manganese additions. At manganese contents of more than 3.5 pct, the effect

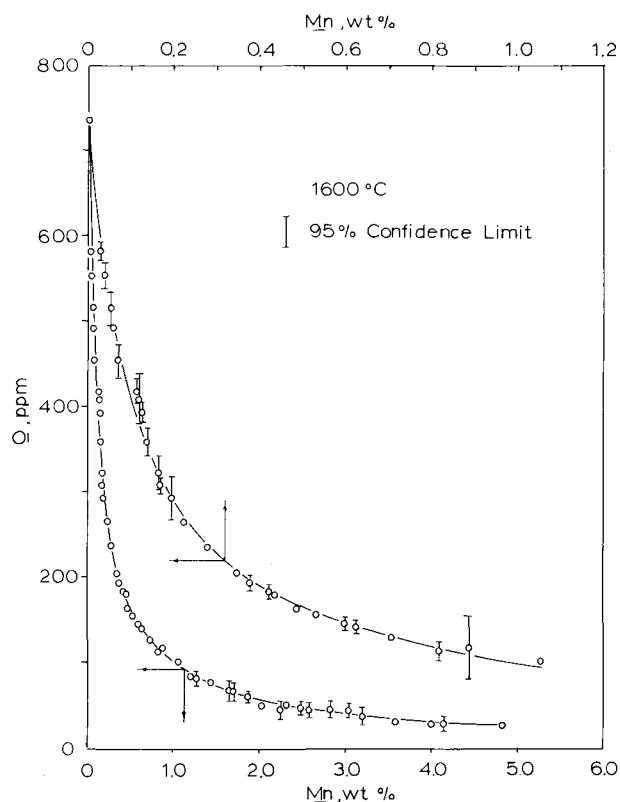


Fig. 2—Effect of manganese on the oxygen content of liquid iron in equilibrium with alumina and spinel solid solutions at 1600°C. The upper line shows the results on an expanded scale.

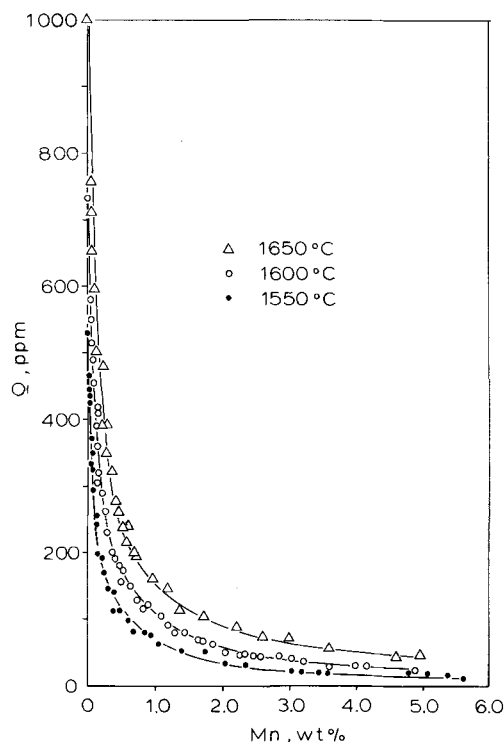


Fig. 3—The effect of manganese on the oxygen content of liquid iron in equilibrium with alumina and spinel solid solutions at several temperatures.

of manganese on the residual oxygen content in liquid iron becomes essentially insignificant.

### Effect of Manganese Variations on the Equilibrium Composition of the Spinel Reaction Product

For proper interpretation of the results obtained during the equilibration experiments, a knowledge of the actual composition of the spinel deoxidation product is essential. With this objective, the composition of thin films of spinel solid solution which formed on the alumina crucible wall during equilibration with the iron-manganese-oxygen alloys, was determined by neutron activation analysis and also by electron microprobe analysis.

The effect of manganese on the composition of the aluminate deoxidation product at 1600°C as determined by both analytical techniques is shown in Fig. 4. From these results it is clear that as manganese content of the iron melt increases, the manganese oxide content of the aluminate spinel also increases, and this is accompanied by an equivalent decrease in the iron oxide content of the deoxidation product until essentially all of the iron in the aluminate has been replaced, and galaxite,  $\text{MnO} \cdot \text{Al}_2\text{O}_3$ , is obtained. For example, at 1600°C, if the manganese content of the iron melt is 0.5 pct, the iron-manganese aluminate spinel will contain 78 mol pct galaxite ( $\text{MnO} \cdot \text{Al}_2\text{O}_3$ ) and 22 mol pct hercynite ( $\text{FeO} \cdot \text{Al}_2\text{O}_3$ ). Again, in a similar manner to that indicated in the previous section, additions of manganese beyond 2.5 pct have little further influence on the composition of the spinel phase. At manganese contents of more than 3.5 pct, the deoxidation products correspond to essentially pure galaxite.

The effect of temperature on the manganese aluminate content of the spinel solid solution is illustrated in Fig. 5. It is evident from this figure that the stability of manganese aluminate in the spinel solid solution decreases with increase in temperature. The stability domains for pure galaxite at 1550, 1600, and 1650°C are found to be at manganese concentrations in excess of 3.0, 3.5, and 4.0 pct respectively.

### Effect of Intermittent Temperature Variations on the Equilibrium Oxygen Content of the Alloy Melt

One experiment was conducted with intermittent variations in operating temperature from a high to a low value and vice versa, in order to investigate the sensitivity of the equilibrium oxygen values to varia-

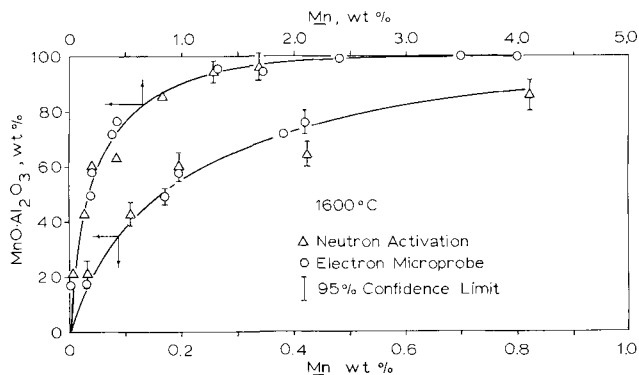


Fig. 4—Effect of manganese on the composition of the deoxidation products,  $(\text{Fe}_x\text{Mn}_{1-x})\text{O} \cdot \text{Al}_2\text{O}_3$ , at 1600°C. The lower line shows the results on an expanded scale.

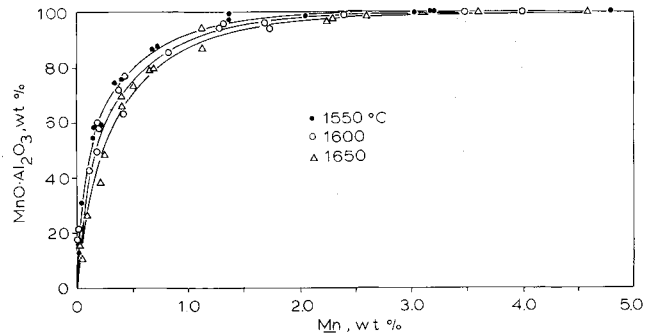


Fig. 5—The effect of manganese on the composition of deoxidation products,  $(\text{Fe}_x\text{Mn}_{1-x})\text{O} \cdot \text{Al}_2\text{O}_3$ , at several temperatures.

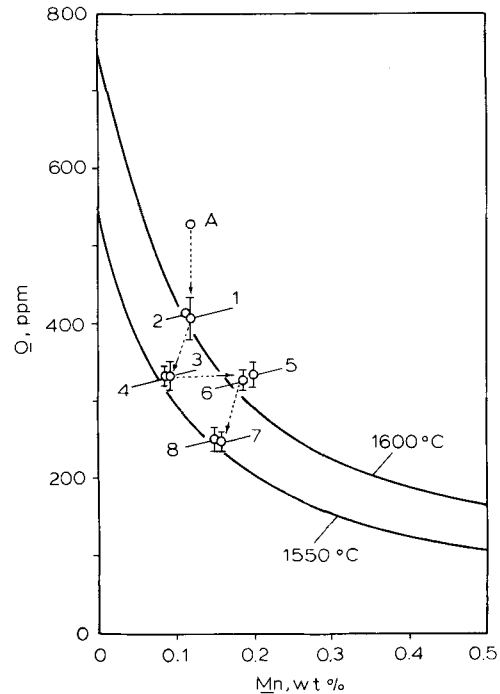


Fig. 6—Equilibration experiment with intermittent variations in operating temperature.

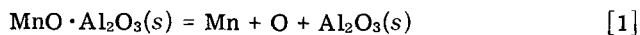
tions in temperature and also to provide a check on the results obtained from the individual experiments conducted at constant temperature. In this particular experiment, a 50 ml alumina crucible was used to contain an alloy melt of approximately 200 g. Approximately 2 g of synthetic spinel compound containing 25 mol pct galaxite and 75 mol pct hercynite was compacted on the crucible base. The results are presented in Fig. 6. The experimental points in this figure were obtained by analysis of suction samples taken at two temperature levels, 1550 and 1600°C. Numbers 1 through 8 show the order in which samples were taken. Point 'A' represents the initial oxygen content of the iron sample. The two solid lines represent the equilibrium relationships determined during the main part of this study, for dissolved oxygen and corresponding manganese contents at temperatures of 1550 and 1600°C. The broken lines show the sequential variations in operating temperature. During the first stage of the experiment at 1600°C, two suction samples, numbers 1 and 2, were taken at time intervals of 3.5 and 5.5 h respectively while holding the melt for a total period of approximately 9 h. The temperature was

then lowered to 1550°C, and two more suction samples, numbers 3 and 4, taken after further time intervals of 3 and 4.5 h for a total heat time at this temperature of 7.5 h. The equilibrium system was then disturbed by adding approximately 15 g of Ferrovac-E together with 3.4 g of 14 pct ferromanganese and raising the operating temperature to 1600°C. The experiment was then continued with the new melt composition at 1600 and 1550°C, repeating the procedures already performed during the first stage of the experiment. During this second stage, suction samples 5 through 8 were withdrawn from the melt. Oxygen analyses of metal sections taken from the rod samples yielded values which were in good agreement with those represented by the solid lines. At the end of the experiment, the composition of the aluminate reaction product attached to the crucible wall, corresponded to a mean value of 57.5 mol pct galaxite, and 42.5 mol pct hercynite. This value is in good agreement with the equilibrium composition of 60 mol pct galaxite, 40 mol pct hercynite calculated from the equilibrium constant for the reaction based on ideal behavior for iron-manganese aluminate spinel solid solutions. This aspect of ideality with respect to the behavior of aluminate spinels is discussed in more detail later.

## DISCUSSION OF RESULTS

### Equilibrium Considerations Pertaining to Galaxite Reactions

The equilibrium constant for the alumina/galaxite reaction,



is given by the equation:

$$K_1 = \frac{a_{\text{O}} \cdot a_{\text{Mn}}}{a_{\text{MnO}} \cdot \text{Al}_2\text{O}_3} \quad [2]$$

where  $a_{\text{O}}$  and  $a_{\text{Mn}}$  are the Henrian activities of oxygen and manganese respectively, based on the hypothetical one wt pct standard state, and  $a_{\text{MnO}} \cdot \text{Al}_2\text{O}_3$  is the Raoultian activity of galaxite based on the pure solid compound as standard state. During the experiments in the present study, the spinel phase was saturated with respect to alumina, and the activity of alumina in Eq. [1] is therefore taken as unity. The equilibrium constant  $K_1$  can be expressed as follows:

$$\begin{aligned} \log K_1 &= \log a_{\text{O}} + \log a_{\text{Mn}} - \log a_{\text{MnO}} \cdot \text{Al}_2\text{O}_3 \\ &= \log f_{\text{O}} + \log [\text{wt pct } \underline{\text{O}}] + \log f_{\text{Mn}} \\ &\quad + \log [\text{wt pct } \underline{\text{Mn}}] - \log a_{\text{MnO}} \cdot \text{Al}_2\text{O}_3 \end{aligned} \quad [3]$$

The activities of oxygen and manganese were calculated from the following relationships:

$$\log f_{\text{O}} = e_{\text{O}}^{\text{O}} [\text{wt pct } \underline{\text{O}}] + e_{\text{O}}^{\text{Mn}} [\text{wt pct } \underline{\text{Mn}}]$$

where:

$$e_{\text{O}}^{\text{O}} = 1750/T + 0.734 \quad (\text{Ref. 26})$$

and,

$$e_{\text{O}}^{\text{Mn}} = -0.02 \quad (\text{Ref. 26}).$$

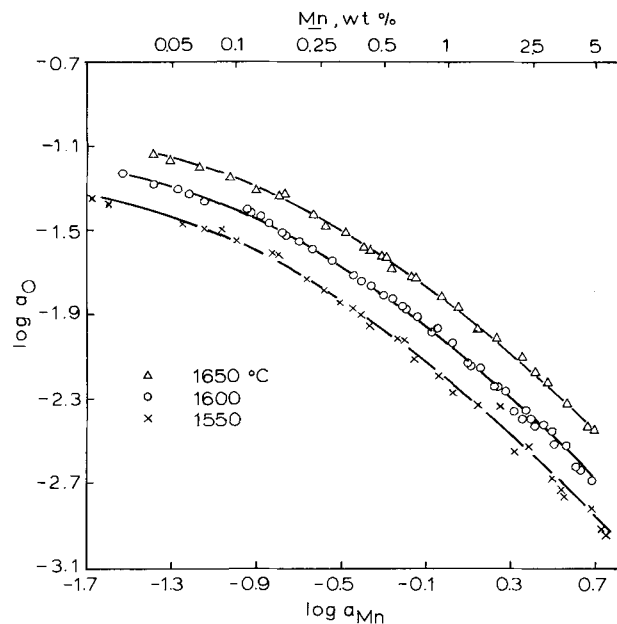


Fig. 7—Manganese and oxygen activities in liquid iron equilibrated with alumina saturated spinel solid solutions.

Also:

$$\log f_{\text{Mn}} = e_{\text{Mn}}^{\text{Mn}} [\text{wt pct } \underline{\text{Mn}}] + e_{\text{Mn}}^{\text{O}} [\text{wt pct } \underline{\text{O}}]$$

where,

$$e_{\text{Mn}}^{\text{Mn}} = 0 \quad (\text{Ref. 26})$$

and,

$$e_{\text{Mn}}^{\text{O}} = -0.083 \quad (\text{Ref. 26}).$$

A plot of  $\log a_{\text{O}}$  against  $\log a_{\text{Mn}}$  should yield a straight line, the slope of which is  $-1$  in that range where the activity of galaxite is unity. Such plots for the three temperature levels, 1550, 1600, and 1650°C, are shown in Fig. 7. At manganese concentrations beyond about 3 pct, the data are in good agreement with this relationship for each temperature. At lower manganese concentrations the lines gradually deviate from linearity due to the decreasing activity of galaxite in the spinel solid solution, which now also contains hercynite. From Eq. [2], it is clear that  $K_1$  is given by the activity product of the solutes when the activity of galaxite is equal to unity. In order to determine precise values for the equilibrium constant, the activity product is plotted in Fig. 8 as a function of the manganese content of the

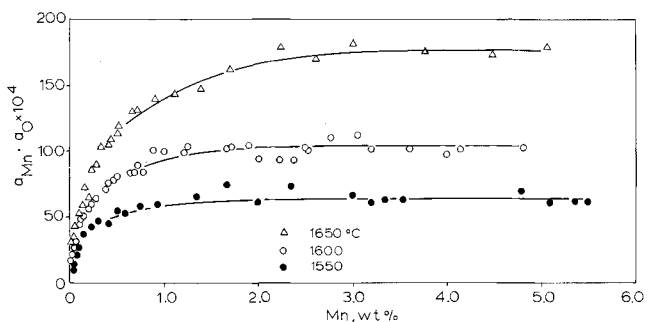


Fig. 8—Effect of manganese on the activity product for equilibrium with alumina saturated spinel solid solutions.

melt. It is clear from this plot that the activity product increases rapidly at low manganese concentrations and reaches a constant value at manganese levels above 3 pct. The values of the activity product in this range correspond to the equilibrium constant. A plot of the logarithm of the equilibrium constant against the reciprocal absolute temperature is shown in Fig. 9. From a least squares analysis of the equilibrium data, the effect of temperature on the equilibrium constant is:

$$\log K_1 = -15,828/T + 6.47 \quad [4]$$

and,

$$\Delta G^\circ = 72,430 - 29.59T \pm 1700 \text{ cal } (\equiv 303,250 - 123.9T \pm 7120 \text{ J}). \quad [5]$$

In an earlier study,<sup>20</sup> the effect of manganese on the deoxidation behavior of aluminum at 1600°C was investigated by equilibrating iron melts containing various amounts of manganese up to 4 wt pct, in alumina crucibles. A value for the equilibrium constant  $K_1$  can be calculated from the earlier data, assuming the activity of galaxite at manganese contents above 3 wt pct is unity. The value obtained at 1600°C is  $-1.98$  logarithmic units, which yields a value for the standard free energy change of 16,970 cal ( $\equiv 71,050$  J). This is in excellent agreement with the value of 17,010 cal ( $\equiv 71,210$  J) obtained in the present work.

The stability of galaxite at steelmaking temperatures can be estimated from the present results by combining the following data with Eq. [5]:

$$\text{Mn}(l) = \underline{\text{Mn}} \text{ (1 wt pct)} \\ \Delta G^\circ = -9.11T \text{ cal } (\equiv -38.14 T \text{ J}) \text{ (Ref. 27)} \quad [6]$$

$$1/2 \text{ O}_2(g) = \underline{\text{O}} \text{ (1 wt pct)} \\ \Delta G^\circ = -28,000 - 0.69T \text{ cal } (\equiv -117,230 - 2.89T \text{ J}) \\ \text{ (Ref. 27)} \quad [7]$$

$$\text{MnO}(s) = \text{Mn}(l) + 1/2 \text{ O}_2(g) \\ \Delta G^\circ = 95,400 - 19.7T \text{ cal } (\equiv 399,400 - 82.5T \text{ J}) \\ \text{ (Ref. 27)}. \quad [8]$$

This yields an expression for the effect of temperature on the free energy of formation of galaxite from its component oxides, *i.e.*,

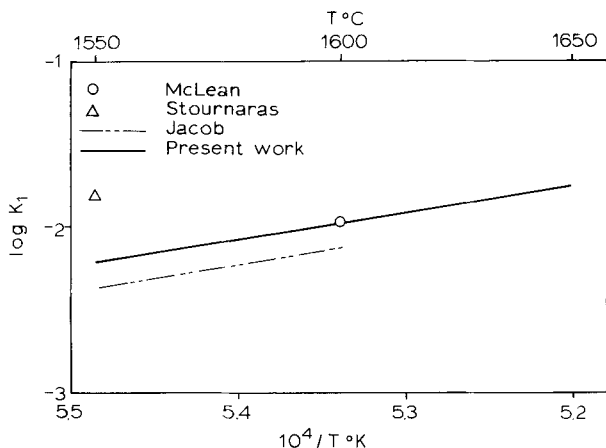
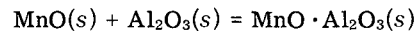


Fig. 9—Comparison of equilibrium data for the reaction:  $\text{MnO} \cdot \text{Al}_2\text{O}_3(s) = \underline{\text{Mn}} + \underline{\text{O}} + \text{Al}_2\text{O}_3(s)$ .



$$\Delta G^\circ = -5030 + 0.09T \pm 2400 \text{ cal } (\equiv -21,060 + 0.38T \pm 10,050 \text{ J}). \quad [9]$$

Combining the data from Eqs. [5] to [7] yields the following expression for the oxygen dissociation pressure of galaxite:

$$\text{MnO} \cdot \text{Al}_2\text{O}_3(s) = \text{Mn}(l) + 1/2 \text{ O}_2(g) + \text{Al}_2\text{O}_3(s) \\ \Delta G^\circ = 100,430 - 19.79T \pm 1700 \text{ cal } (\equiv 420,480 - 82.9T \pm 7100 \text{ J}) \text{ (1550 to 1650}^\circ\text{C)} \quad [10]$$

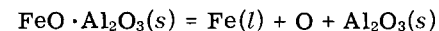
and,

$$\log P_{\text{O}_2} = -43,894/T + 8.65. \quad [11]$$

At 1600°C, the oxygen dissociation pressure is  $1.64 \times 10^{-15}$  atm, which is in good agreement with the value of  $1.15 \times 10^{-15}$  atm calculated from the data reported by Jacob.<sup>21</sup>

#### Thermodynamic Behavior of Iron-Manganese Aluminate Spinels

Substituting the equilibrium constant,  $K_1$ , together with the equilibrium values for the activities of oxygen and manganese, at each temperature level in Eq. [2], yields values for the activity of galaxite in the deoxidation product. The values for the activity of galaxite thus calculated are plotted against the mole fraction of galaxite in the deoxidation product, as determined by chemical analysis, in Fig. 10 and it is clear that for the temperatures investigated, the iron-manganese aluminate spinels obey Raoult's Law. This ideal behavior was further substantiated by calculation of the activity of hercynite in the spinel deoxidation product at each temperature level investigated. The activity of hercynite in the spinel solid solution,  $(\text{Fe}_x\text{Mn}_{1-x})\text{O} \cdot \text{Al}_2\text{O}_3$ , was calculated by incorporating the present data for the oxygen activities in the equilibrium expressions for hercynite formation reported previously by Kim and McLean:<sup>15</sup>



for which,

$$\log K_2 = -9575/T + 3.98 \quad [12]$$

where,

$$K_2 = \frac{a_{\text{O}} \cdot a_{\text{Fe}}}{a_{\text{FeO} \cdot \text{Al}_2\text{O}_3}}$$

The activity of alumina is again taken as unity and the activity of iron in the Fe-Mn alloys is set equal to the mole fraction. The values for the activity of hercynite thus calculated are plotted against the mole fraction of hercynite as determined by chemical analysis. These results are included in Fig. 10. Again it is evident that the iron-manganese aluminate solid solutions obey Raoult's Law at steelmaking temperatures. The excellent agreement between the two sets of data for the behavior of spinel solid solutions is further confirmation of the internal consistency not only of the results obtained during the present study, but also of those de-

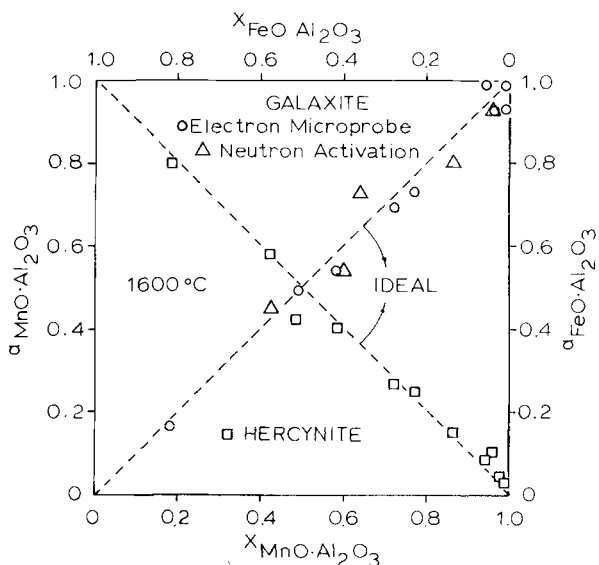
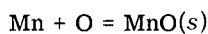


Fig. 10—Relationship between activities and mole fractions of galaxite or hercynite in the solid solutions at 1600°C.

terminated during the previous investigation on the stability of hercynite in the absence of manganese.

The activity of manganese oxide in alumina saturated spinel was estimated from the equilibrium constant for the following reaction:



$$K_3 = a_{\text{MnO}} / a_{\text{Mn}} \cdot a_{\text{O}} \quad [13]$$

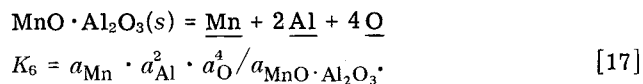
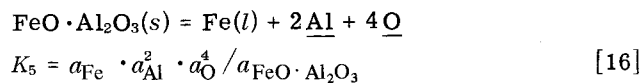
where,

$$\log K_3 = 14,450/T - 6.43 \quad (\text{Ref. 27}). \quad [14]$$

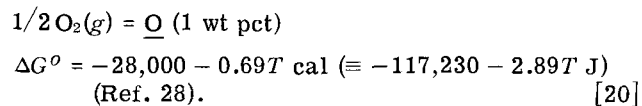
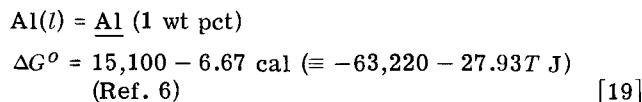
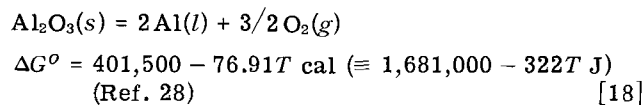
From the equilibrium constant together with the solute activities in liquid iron, values were calculated for the activity of manganese oxide at each temperature level investigated. These manganese oxide activities are plotted against the mole fraction in Fig. 11, from which it is evident that a strong negative deviation from Raoult's Law exists in the system. In a similar fashion, iron oxide activities in the mixed oxide spinel were calculated and plotted against the mole fraction in Fig. 12. Again it is clear that the activity of iron oxide in the alumina saturated spinel shows a strong negative deviation from Raoult's Law.

#### Formation of Spinel Compounds During Deoxidation of Steel with Manganese and Aluminum

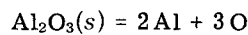
When liquid iron containing dissolved oxygen is deoxidized by aluminum in either the absence or presence of manganese, the various equilibria can be represented as follows:



The deoxidation constant  $K_4$  for the reaction in which the deoxidation product is alumina can be calculated from the following data:



Combining these equations, the free energy change for the reaction:



is given by:

$$\Delta G^\circ = 287,300 - 92.32T \text{ cal } (\equiv 1,202,900 - 386.5T \text{ J}) \quad [21]$$

and,

$$\log K_4 = -62,780/T + 20.17. \quad [22]$$

When the results for the stability of hercynite in the absence of manganese, Eq. [12], are combined with Eq. [22], the deoxidation constant for the hercynite reaction:

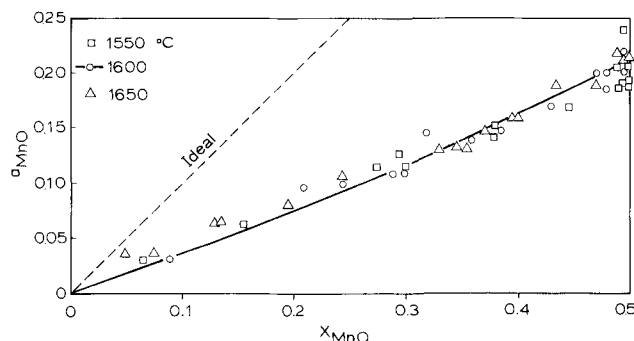


Fig. 11—Relationship between the activity and mole fraction of manganese oxide in the iron-manganese aluminate spinel, saturated with respect to alumina.

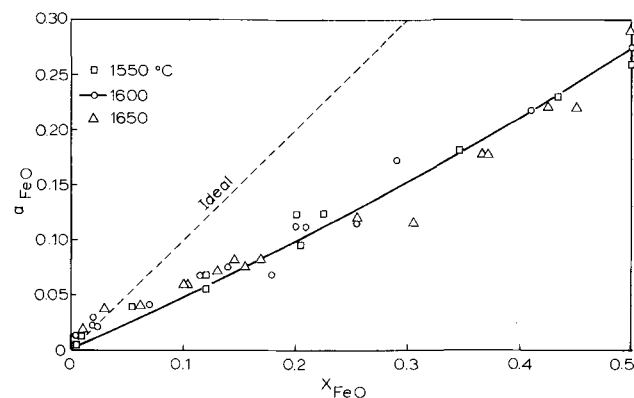
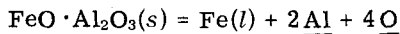


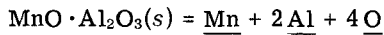
Fig. 12—Relationship between the activity and mole fraction of iron oxide in the iron-manganese aluminate spinel, saturated with respect to alumina.



is given by:

$$\log K_5 = -72,360/T + 24.16. \quad [23]$$

When the results of the present work, in the presence of manganese, Eq. [4], are combined with Eq. [22], the deoxidation constant for the galaxite reaction:

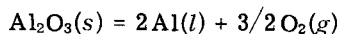


is given by:

$$\log K_6 = -78,611/T + 26.64. \quad [24]$$

Using Eqs. [22] to [24] a deoxidation diagram has been constructed which shows the relationship between the activities of aluminum and oxygen dissolved in either liquid iron or liquid iron-manganese alloys, when the melt is in equilibrium with either spinel compounds or alumina. The deoxidation diagram for a temperature of 1600°C is shown in Fig. 13. The line in the upper left corner of the diagram represents the aluminum-oxygen relationship in the absence of manganese when the deoxidation product is hercynite. Lines 1 through 5 correspond to the aluminum-oxygen relationships for manganese concentrations between 0.25 and 4 wt pct where the deoxidation products are iron-manganese aluminates of increasing manganese content. Above 3.5 pct manganese, the spinel compound is essentially pure galaxite. When the deoxidation product is an aluminate, manganese increases the deoxidation power of aluminum in two ways. First, by decreasing the activity of alumina in the spinel phase, and second, by reducing the oxygen potential of the reaction product.

Similar calculations have been made using the most recent data of Ghosh and Kay<sup>29</sup> for the stability of alumina:



$$\Delta G^\circ = 398,560 - 80T \text{ cal } (\equiv 1,668,700 - 335T \text{ J}). \quad [25]$$

At 1600°C, Eq. [25] yields a value for  $\Delta G^\circ$ , of 249 kcal ( $\equiv 1043$  kJ). This may be compared with the value of 257 kcal ( $\equiv 1076$  kJ) from Eq. [18]. The effect of this free energy difference on the aluminum deoxidation diagram is shown by the broken lines in Fig. 14. For oxygen activities corresponding to the critical points with hercynite, and galaxite at the 4 pct Mn level, the equivalent aluminum activities are increased by 0.51 logarithmic units at each critical point. On a concentration basis, this is equivalent to a change in the aluminum residual for equilibrium with hercynite of less than 1 ppm. In the case of equilibrium with galaxite, the critical aluminum concentration is increased from 19 to 62 ppm.

Figure 15 summarizes the effects of manganese on the deoxidation behavior of aluminum at 1600°C. The line denoted by 'O' shows the effect of manganese on the critical oxygen content of the steel, above which the deoxidation products are aluminates, and below which the stable phase is alumina. The 'MnO · Al<sub>2</sub>O<sub>3</sub>' line depicts the enrichment in manganese oxide content of the aluminate spinel with increasing manganese concentration in the melt. From the equilibrium relationship between aluminum and oxygen in the presence of manganese as expressed in Eq. [24], the effect of

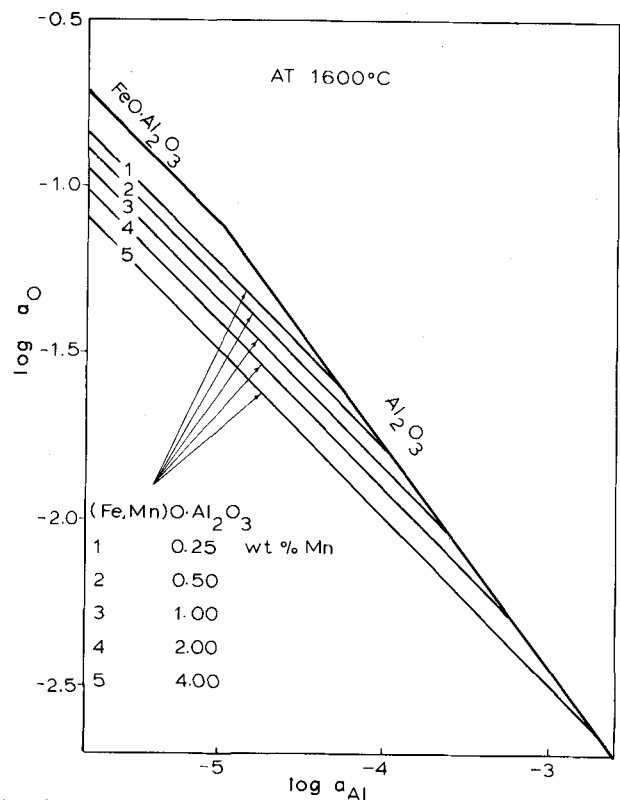


Fig. 13—Equilibration diagram for aluminum deoxidation in the presence of various concentrations of manganese.

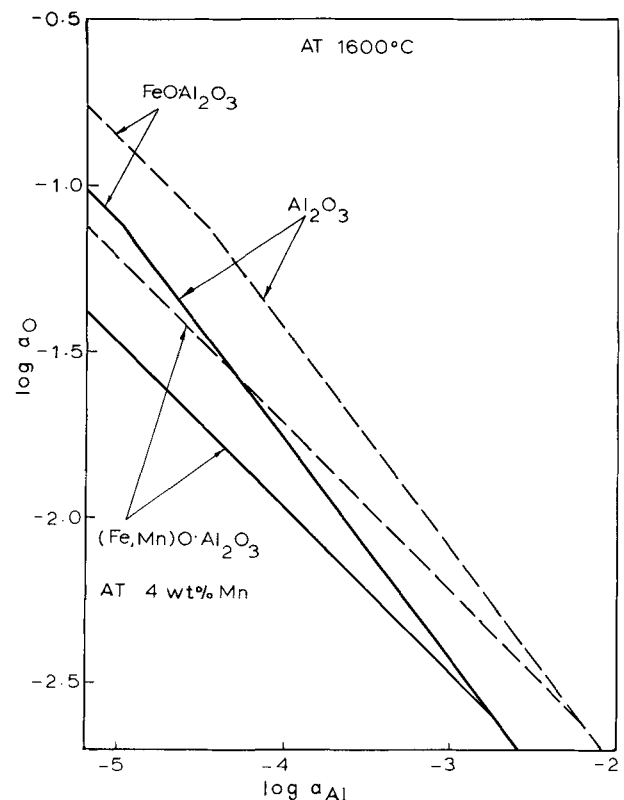


Fig. 14—Aluminum deoxidation diagram, in which the broken lines represent the values calculated using Ghosh and Kay's<sup>29</sup> data for the reaction:  $\text{Al}_2\text{O}_3(s) = 2\text{Al}(l) + 3/2\text{O}_2(g)$ .

manganese on the critical aluminum content of the steel can be calculated when equilibrium has been established with alumina and aluminate compounds. This relation-



ship is shown in the figure by the line marked 'Al'. The dissolved aluminum concentrations thus predicted are compared with the values obtained by actual analysis of the high manganese melts, which are illustrated in the figure by the triangle points. These points are located above the 'Al' line. However, considering the extended scale of this diagram, and also the extremely small residual concentrations, the agreement is satisfactory. For example, at a manganese concentration of 4.8 pct, the predicted value of the dissolved aluminum concentration is 26 ppm while the value determined by chemical analysis is 38 ppm. It is interesting to note that this latter value is about 40 ppm below that which would be predicted if the data of Ghosh and Kay<sup>29</sup> were used to calculate the aluminum residual. For residual aluminum concentrations which lie above the 'Al' line, the composition of the inclusion phase will be pure alumina. For aluminum concentrations below the line, the deoxidation product will be aluminate spinel, the composition of which will depend on the manganese content of the steel. When the deoxidation product is alumina, manganese simply acts as an alloying element and has no effect on the deoxidation behavior of aluminum.

The sequence of reactions which occur when the aluminum is added to molten steel will depend on the oxygen and manganese contents at the time of the addition. For example, if the steel composition is below the critical oxygen line in Fig. 16 when aluminum is added, the deoxidation product is alumina. In this case subsequent additions of manganese would play no part in the deoxidation process, and manganese would simply behave as an alloying element. If the steel composition lies above the line, additions of aluminum will cause the precipitation of aluminates. The steel com-

position will shift towards the line, and then move downwards along this phase boundary. During this period the aluminates become unstable, alumina is formed and manganese and oxygen return to the steel. Simultaneously, aluminum reacts with oxygen to precipitate alumina. With the elimination of aluminates, the steel composition will move away from the phase boundary and into the alumina field.

In actual practice following the precipitation of aluminates, some will separate into the slag phase or into the ladle glaze, some will decompose as described previously, others will become coated with solid alumina which will prevent any further oxygen transfer from the aluminates back into the steel. These alumina covered spinels are thus effectively isolated from subsequent compositional changes within the molten steel. Under these conditions further reaction between aluminum and oxygen dissolved in liquid steel will result in the precipitation of alumina.

With respect to the sequence of reactions occurring during deoxidation with manganese and aluminum, Straube *et al*<sup>18</sup> have reported that iron-manganese aluminates are often enclosed within envelopes of alumina. Similar observations have been reported more recently by Venkatadri<sup>30</sup> based on experiments conducted with 90 kg melts held under argon and deoxidized with aluminum and manganese. Venkatadri also found that in the presence of high aluminum residuals (>0.05 pct), the spinel reaction products were progressively reduced to alumina after periods of about 5 to 8 min. All of these observations are in accord with the sequential reactions shown schematically in Fig. 16.

It is also worth noting that during pouring of steels containing aluminum and manganese, reoxidation reac-

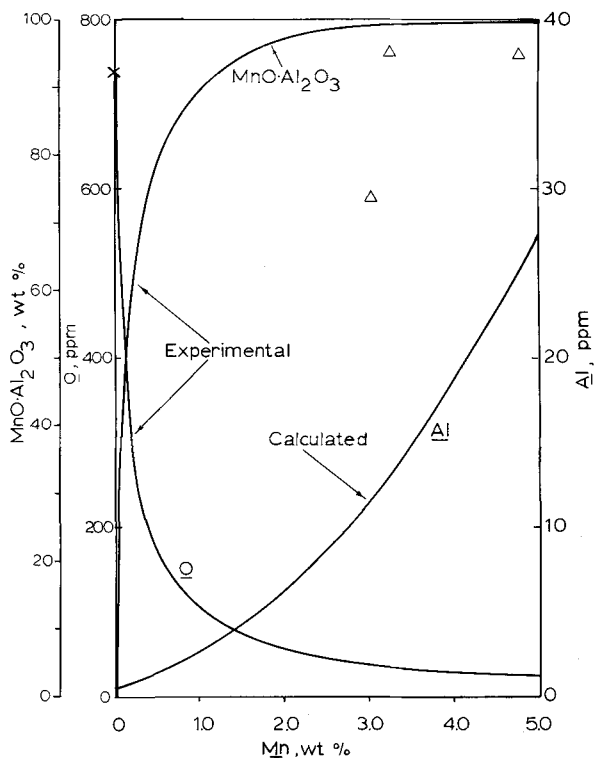


Fig. 15—Effect of manganese on the composition of liquid iron melts and the corresponding spinel deoxidation products at 1600°C. Triangles correspond to measured aluminum concentrations.

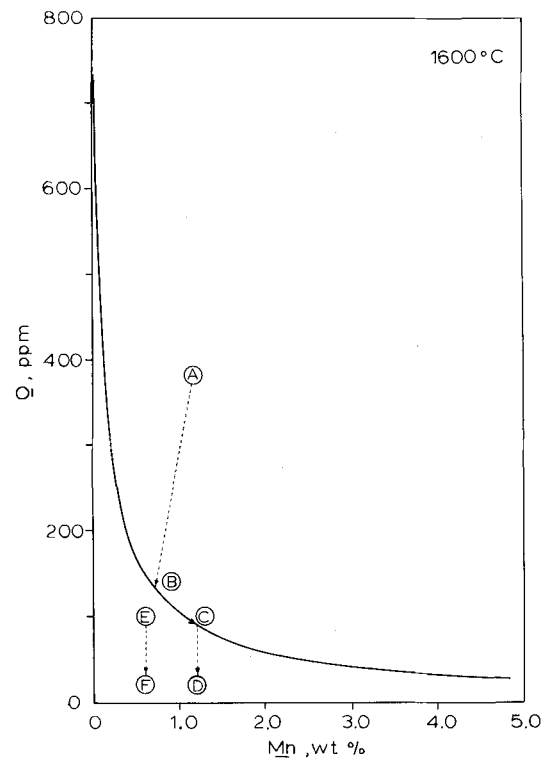


Fig. 16—Sequential deoxidation reaction paths. A-B: Aluminate precipitation. B-C: Aluminate decomposition and Alumina precipitation. C-D and E-F: Alumina precipitation.

tions can lead to the formation of alumina followed by iron-manganese aluminates. In this case the reaction products are generally very much larger, and, in the presence of silicon, frequently contained within an iron-manganese aluminosilicate matrix. Examples of spinel inclusions formed by reoxidation have been described in detail by Luyckx *et al.*<sup>1</sup>

In a continuation of the present work, the effects of up to 20 pct chromium on the residual oxygen concentration in steel and on the composition of various spinel reaction products, has been investigated. The results of this study have been reported in a separate paper.<sup>31</sup>

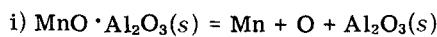
### CONCLUSIONS

From the experimental study for the equilibration reaction between liquid iron-oxygen alloys containing manganese concentrations up to 6 pct and alumina/galaxite at steelmaking temperatures, the following conclusions are drawn.

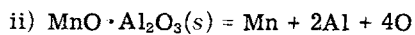
1) With increasing manganese concentrations, the equilibrium oxygen content rapidly decreased. For example, at 1600°C the equilibrium oxygen level falls from 740 ppm in the absence of manganese to 165 ppm in the presence of 0.5 pct manganese. At manganese contents of more than 3.5 pct, the effect of manganese on the residual oxygen content in liquid iron becomes essentially insignificant.

2) Effect of manganese variations in the liquid iron on the composition of the aluminate deoxidation product as determined with electron microprobe and neutron activation analysis indicated that the manganese oxide content of the aluminate spinel increases with increasing manganese concentrations of the iron melt, and this is accompanied by an equivalent decrease in the iron oxide content of the deoxidation product. At manganese contents of more than 3.5 pct at 1600°C, the deoxidation product corresponded to essentially pure galaxite.

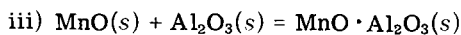
3) From the experimental results, the following thermodynamic relationships have been established for temperatures between 1823 and 1923 K:



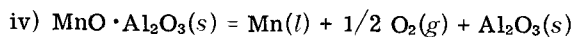
$$\Delta G^\circ = 72,430 - 29.59T \pm 1.7 \text{ kcal} \\ (\equiv 303,250 - 124T \pm 7.1 \text{ kJ})$$



$$\Delta G^\circ = 359,730 - 121.9T \pm 1.9 \text{ kcal} \\ (\equiv 1,506,120 - 510T \pm 8 \text{ kJ})$$



$$\Delta G^\circ = -5030 + 0.09T \pm 2.4 \text{ kcal} \\ (\equiv -21,060 + 0.38T \pm 10 \text{ kJ})$$



$$\Delta G^\circ = 100,430 - 19.79T \pm 1.7 \text{ kcal} \\ (\equiv 420,480 - 82.9T \pm 7.1 \text{ kJ})$$

4) For the temperatures investigated, the iron-manganese aluminate spinels,  $(\text{Fe}_x\text{Mn}_{1-x})\text{O} \cdot \text{Al}_2\text{O}_3$ , were found to obey Raoult's Law.

5) The activities of manganese oxide and iron oxide in alumina saturated spinel exhibited strong negative

deviations from Raoult's Law.

6) Using the data from the present investigation together with others available in the literature, deoxidation diagrams have been constructed which show the relationships between the activities of aluminum and oxygen dissolved in liquid iron, when the melt is in equilibrium with either iron-manganese aluminate spinels or alumina.

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