Sulfides and Oxides in Fe-Mn Alloys: Part I. Phase Relations in Fe-Mn-S-O System

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This is a critical review of available equilibrium data between phases involving Fe, Mn, S, and O. Using the Morey-Williamson theorem, and that modified by Darken, the sulfur and oxygen potential diagrams are constructed for the Fe-S-O system involving nine univariant and three invariant equilibria. The solubility of sulfur in wustite-saturated iron is evaluated; the sulfur content of iron in equilibrium with wustite and liquid oxysulfide reaches a maximum of 143 ppm at 1200°C; this is about one half of that corresponding to the solidus of the Fe-S system. An estimate is made of the phase equilibria in the Fe-Mn-S-O quaternary system involving gamma iron and Mn(Fe)O phases. There is a eutectic invariant at ~900°C, and the liquid miscibility gap invariant is estimated to be at ~1225°C. From the expected phase relations and equilibria, it is deduced that if sufficient oxygen and sulfur, *i.e.* Mn(Fe)O and Mn(Fe)S phases, are present in Fe-Mn alloys, there may be a liquid oxysulfide phase present at temperatures above 900°C, depending on the concentration of manganese in solution. The higher the manganese content in solution, the higher is the temperature above which a liquid phase is present, *e.g.* for 10 ppm Mn, 900°C and for ~90 pct Mn, ~1225°C. A mechanism is suggested for the precipitation of sulfides and oxysulfides near the surface of steel during heating in an oxidizing atmosphere. In the Appendix by Darken and Gurry, results are given of the melting temperatures of mixtures of wustite and pyrrhotite in equilibrium with iron, from an investigation carried out about thirty years ago.

HOT-SHORTNESS of steel is an old metallurgical problem that has been a subject of research for several decades. It has long been recognized that the presence of oxygen and, particularly, of sulfur in steel is the primary cause of hot-shortness which usually occurs within the temperature range 900° to 1100°C. The hot-short range, of course, varies with the type of steel, particularly with the pct Mn/pct S ratio of the steel. In fact, for a long time manganese has been used to counteract the deleterious effect of sulfur in an attempt to render steels less susceptible to hot-shortness. There are many papers to be found in the technical literature on this subject; however, a survey of past work on hot-shortness is outside the scope of the present paper.

Since Mn, S, and O are often associated with the occurrence of hot-shortness, or absence thereof, we decided to reexamine the chemistry of reactions involving Mn, S, and O in solid steel over a wide temperature range. In the first part of the paper, we shall discuss the thermodynamics of the quaternary system Fe-Mn-S-O; and in the second part, we shall discuss and demonstrate experimentally the conditions for the formation of liquid oxysulfides during oxidation of steels containing sulfur.

Some information is available in the technical literature on equilibrium relations in simple and complex systems involving Fe, Mn, S, and O. In order to collate the available equilibrium data and present it in a condensed form, much use will be made of the theorem on univariant curves intersecting at an invariant point in pressure or activity vs temperature plots.

THEOREM ON UNIVARIANT CURVES INTERSECTING AT AN INVARIANT POINT

A theorem was developed by Roozeboom and Schreinemakers[1] (later discussed further in other papers)[2,3] on the relation of the univariant curves intersecting at an invariant point in a pressure vs temperature (P-T) plot for ternary systems. A more general form of this theorem was later developed by Morey and Williamson[4] for multicomponent systems; the subject was later reviewed by Morey.[5] Darken[6] gave a constructive illustration of the application of this theorem to ternary systems and its application to the Fe-Si-O system. A similar study was made later by Turkdogan[7] in deriving oxygen potentials and phase equilibria in the Fe-Ca-O ternary system. Also Kullerud and Yoder[8] discussed the application of this theorem to phase relations in binary systems where pressure is a variable.

The Morey-Williamson theorem initially developed for P-T curves about an invariant equilibrium was later adapted by Darken[9] to the thermodynamic activity, *a*, vs temperature relations. That is, the relation between the variations in activity and temperature in any univariant system is given in the form of a determinant, which for a ternary system reduces to

$$\left.\frac{\partial \ln a_3}{\partial(1/T)}\right|_p = \frac{1}{R}\,\frac{\begin{vmatrix} m_1' & m_2' & \Delta H' \\ m_1'' & m_2'' & \Delta H'' \\ m_1''' & m_2''' & \Delta H''' \end{vmatrix}}{\begin{vmatrix} m_1' & m_2' & m_3' \\ m_1'' & m_2'' & m_3'' \\ m_1''' & m_2''' & m_3''' \end{vmatrix}} \qquad [1]$$

For any univariant equilibrium at constant pressure,

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Eq. [1] reduces to the familiar form

$$\left.\frac{\partial \ln a_3}{\partial(1/T)}\right|_p = \frac{\Delta H}{R} \qquad [2]$$

where R is the gas constant and ΔH is the enthalpy change accompanying the reaction. It is convenient to use $RT \ln a$ vs T plots from which $d \ln a/d\ (1/T)$ is obtained by

$$\frac{d \ln a}{d(1/T)} = T \ln a - \frac{Td(T \ln a)}{dT} \qquad [3]$$

In the determinant the units for mass, m, and the enthalpies of phases $\Delta H'$, $\Delta H''$, . . . must be interconsistent. A convenient form for mass is the atomic ratio m_2/m_1, m_3/m_1, . . . and the enthalpy is then per g-atom of component 1.

For a quaternary system the compositions of six phases of an invariant equilibrium are given in a three-dimensional diagram, *i.e.* a tetrahedron, each corner representing one of the components. Depending on the composition of the phases, the polyhedron constructed for an invariant equilibrium may be an octahedron, a hexahedron, or a tetrahedron. In all cases, there are twenty planes where three phases are coplanar; ten planes merge at the composition of every phase and four planes intersect at a line joining the compositions of two phases. Needless to say, the application of the Morey-Williamson theorem, or that as modified by Darken, to quaternary systems is complex and cumbersome. Since little is known about the phase equilibria in the Fe-Mn-S-O or other quaternary systems, further discussion of the application of the theorem to quaternary systems is not warranted at present.

Fe-S-O TERNARY SYSTEM

In the context of the present study, the ternary Fe-S-O system is an important part of the Fe-Mn-S-O quaternary; therefore this ternary system will be discussed first in some detail. The thermodynamics of this system is known with sufficient degree of accuracy. By excluding ferric oxide, pyrite, the sulfate phases and ignoring the $\alpha \rightarrow \gamma \rightarrow \delta$ phase transformations in iron, there are six condensed phases: gamma iron (γ), wustite (W), magnetite (M), pyrrhotite (P), liquid oxysulfide (l_1) and metallic liquid (l_2). With these phases a maximum of twenty univariant equilibria involving fifteen invariant points are possible. Of these, however, there are only three stable invariant points involving nine univariant equilibria. The tenth stable univariant is for the liquid miscibility gap[10] (γ, l_1 and l_2) which starts from the Fe-O binary side at 1527°C and terminates at ~1345°C in the ternary liquid containing 81 pct Fe, 17 pct S, and 2 pct O.

Table I. Data for Invariant Equilibria in Fe-S O System

Invariant Equilibria	p_{O_2}, atm	p_{S_2}, atm	$-RT\ln p_{O_2}$ kcal	$-RT\ln p_{S_2}$ kcal
I. 560°C Iron, wustite, magnetite, pyrrhotite, gas	4.8×10^{-27}	5.5×10^{-14}	100.3	50.5
II. 915°C Iron, wustite, pyrrhotite, liquid (1), gas	3.2×10^{-17}	2.2×10^{-8}	89.6	41.6
III. 942°C Wustite, magnetite, pyrrhotite, liquid (1), gas	1.1×10^{-14}*	5.4×10^{-6}*	77.6	29.3

Composition of l_1 at 915°C: $N_{Fe} = 0.50$, $N_O = 0.19$, $N_S = 0.31$.
Composition of l_1 at 942°C: $N_{Fe} = 0.49$, $N_O = 0.19$, $N_S = 0.32$.

*$a_{Fe} = 0.09$.

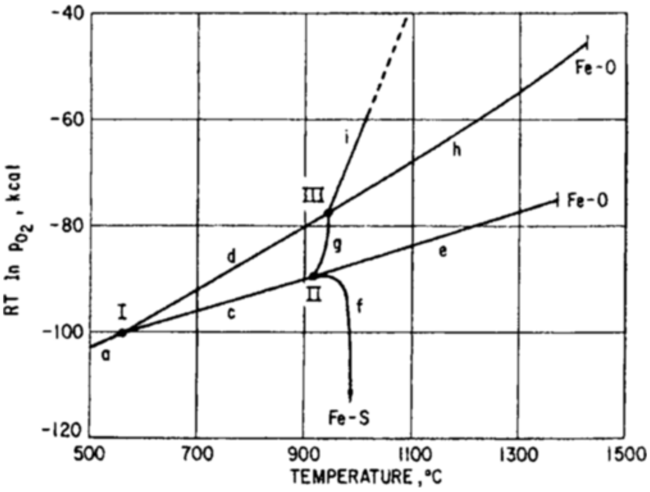

Fig. 1—Oxygen potentials for univariant equilibria in Fe-S-O system. *a)* Iron, magnetite, pyrrhotite; *b)* iron, wustite, magnetite; *c)* iron, wustite, pyrrhotite; *d)* wustite, magnetite, pyrrhotite; *e)* iron, wustite, liquid (1); *f)* iron, pyrrhotite, liquid (1); *g)* wustite, pyrrhotite, liquid (1); *h)* wustite, magnetite, liquid (1); *i)* magnetite, pyrrhotite, liquid (1).

The data compiled on three invariant points for this system are summarized in Table I; particular details on each invariant are given below.

Invariant I at 560°C

The equilibrium phases at this invariant point are: iron (undercooled γ-phase), wustite, magnetite and pyrrhotite. The temperature of this invariant has not been measured; however, this is not expected to differ much from 560°C which is for the Fe-O binary system. Because of the negligible mutual solid solubilities between pyrrhotite and iron oxides, the oxygen activity of wustite and magnetite can be assumed not to be changed much by the presence of pyrrhotite; similarly, the sulfur activity will not be much affected by the presence of iron oxides. Therefore, the values of p_{O_2} and p_{S_2} for iron-wustite-magnetite and iron-pyrrhotite may be used for this invariant. The oxygen potentials used are those measured by Darken and Gurry.[11] The sulfur potentials for the iron-pyrrhotite equilibrium measured by Rosenqvist[12] are in close agreement with other data compiled by Richardson and Jeffes;[13] these values are used in the present work.

Invariant II at 915°C

Four phases in equilibrium at this invariant point are: gamma iron, wustite, pyrrhotite and liquid oxysulfide. According to Hilty and Crafts,[10] this ternary eutectic temperature is 920°C; Naldrett[14] observed it to be 915°C; according to the previously unpublished work of Darken and Gurry (given in the Appendix), it is 908°C. An average value of 915°C is taken as the invariant temperature. These investigators reported values for the composition of the eutectic liquid which are in good agreement with one another; the selected average composition in at. pct is 50 pct Fe, 31 pct S, and 19 pct O, which is slightly high in iron relative to the "FeO"-"FeS" line in the composition diagram.

Invariant III at 942°C

The equilibrium phases for this invariant are: wustite, magnetite, pyrrhotite and liquid oxysulfide. According to Hilty and Crafts,[10] the peritectic invariant temperature is 950°C; Naldrett[14] gives 934°C. An average temperature of 942°C is taken for this invariant point. The average composition of the peritectic liquid given by these investigators is, in at. pct, 49 pct Fe, 32 pct S, and 19 pct O; in the composition diagram, this point falls between the lines joining "FeO" to "FeS" and "Fe_3O_4" to "FeS".

For the wustite-magnetite equilibrium at 942°C, the iron activity is 0.09 (relative to γ-iron).[11] The value of $p_{S_2} = 5.4 \times 10^{-6}$ atm given in Table I is for pyrrhotite in equilibrium with iron at $a_{Fe} = 0.09$.

Oxygen and Sulfur Potentials

The oxygen and sulfur potentials for the univariant equilibria involving three invariant points in the Fe-S-O ternary system are given in Figs. 1 and 2. Because of the low sulfur solubility in wustite, the univariants c and e in Fig. 1 are linear extensions of one another, because of the composition colinearity of iron, wustite, and oxygen. For similar reasons, in the vicinity of the invariant point III, the univariant h is an extension of d. According to the work of Rosenqvist and Hartvig,[15] the univariant i involving condensed phases magnetite, pyrrhotite and liquid oxysulfide is in equilibrium with 1 atm SO_2 at 1010°C. The equilibrium value $p_{O_2} = 4.5 \times 10^{-11}$ atm, and $p_{S_2} = 4.5 \times 10^{-2}$ atm, thus computed, are used in drawing the line for this univariant from the invariant III in Figs. 1 and 2. The univariants e and h in Fig. 1 terminate at the Fe-O invariant temperatures 1371° and 1424°C, respectively. Because of the low oxygen solubility in pyrrhotite, the lines for univariant equilibria a, c, and f, in Fig. 2 are an extension of each other. For the same reason the univariant b is drawn vertical at 560°C in Fig. 2 but does not appear in Fig. 1.

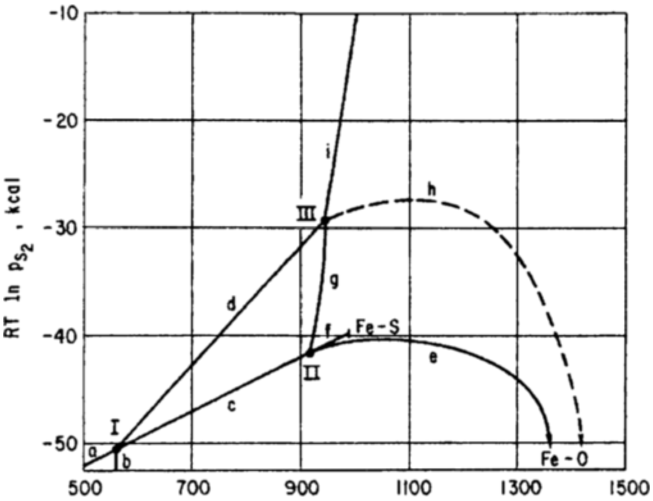

Fig. 2—Sulfur potentials for univariant equilibria in the Fe-S-O system. *a*) Iron, magnetite, pyrrhotite; *b*) iron, wustite, magnetite; *c*) iron, wustite, pyrrhotite; *d*) wustite, magnetite, pyrrhotite; *e*) iron, wustite, liquid (1); *f*) iron, pyrrhotite, liquid (1); *g*) wustite, pyrrhotite, liquid (1); *h*) wustite, magnetite, liquid (1); *i*) magnetite, pyrrhotite, liquid (1).

Qualitative application of the Morey-Williamson theorem predicts that the univariant g at the invariant point III in Figs. 1 and 2 has a negative slope with the stable part in the direction of increasing temperature. However, if the liquid composition is colinear with that of wustite and pyrrhotite, the curve g will have an infinite slope at 942°C. At the invariant point II, it has a positive slope. Therefore, the univariant g has either a temperature maximum, or approaches III with an infinite slope, if the compositions of wustite, pyrrhotite and liquid (1) are colinear at 942°C. The univariants e and h in Fig. 2 have positive (or zero) slopes with metastable extensions being above the univariants c and d, respectively. The positions of univariants e, h, and g in Fig. 2, and f and g in Fig. 1 can be computed from the enthalpy of formation of the liquid oxysulfide, ΔH_l; however, since no measured value of ΔH_l is available, it should be evaluated from other data in Fig. 2 by the application of the theorem.

Enthalpy of Formation of Liquid Oxysulfide

In conjunction with the oxygen and sulfur potential diagrams in Figs. 1 and 2, the enthalpies used in the calculations (from elements in their standard states at the temperature considered) are given in Table II; the data for the oxides are from Darken and Gurry[11] and those for pyrrhotite from Burgmann *et al.*[16]

The determinant for the slope of univariant e at the invariant temperature 915°C involving iron, wustite, liquid (1) and gas is given by

$$\frac{d \ln a_S}{d(1/T)} = \frac{1}{R} \frac{\begin{vmatrix} 1 & 0 & 0 \\ 1 & 1.055 & -67.22 \\ 1 & 0.38 & \Delta H_l \end{vmatrix} \begin{array}{l} \text{Fe} \\ W \\ l_1 \end{array}}{\begin{vmatrix} 1 & 0 & 0 \\ 1 & 1.055 & 0 \\ 1 & 0.38 & 0.62 \end{vmatrix} \begin{array}{l} \text{Fe} \\ W \\ l_1 \end{array}} \qquad [4]$$

Remembering that the sulfur activity $a_S \propto (p_{S_2})^{1/2}$, the slope $d\,RT \ln p_{S_2}/dT = 0.0175$ kcal per deg for e at 915°C in Fig. 2.(the derivation of this univariant is discussed in the next section) gives $d \ln a_S/d(1/T) = -31.2/R$. Inserting this in Eq. [4] gives $\Delta H_l = -43.5$ kcal per g-atom Fe. The composition of the liquid may be approximated as 0.38 FeO · 0.62 FeS. Assuming an ideal solution, the enthalpy of this liquid may be calculated from the enthalpies of molten wustite and pyrrhotite giving ΔH_l(ideal) = −38 kcal per g-atom Fe.

The slope of the univariant i at 942°C in Fig. 1 for magnetite-pyrrhotite-liquid (1) equilibrium, $d\,RT \ln p_{O_2}/dT = 0.25$ kcal per deg, gives $d \ln a_O/d$ $d \ln a \;\;/d(1/T) = -190.8/R$. From the determinant for this univariant equilibrium

Table II. Available Enthalpy Data Used to Compute the Enthalpy of Liquid Oxysulfide (From Elements in Their Standard States at the Temperature Considered) by Applying Morey-Williamson Theorem to Data in Figs. 1 and 2

Invariant Temperature, °C	Phase Composition				Enthalpy, kcal per g-atom Fe			
	Magn.	Wust.	Pyrr.	Liquid	Magn.	Wust.	Pyrr.	Liquid
915	Fe_3O_4	$Fe_{0.947}O$	FeS	$FeO_{0.38}S_{0.62}$	−87.0	−67.32	−36.1	−43.5
942	Fe_3O_4	$Fe_{0.885}O$	$Fe_{0.99}S$	$FeO_{0.388}S_{0.654}$	−87.0	−72.09	−32.9	−36.4

univariant equilibrium

$$-190.8 = \frac{\begin{vmatrix} 1 & 0 & -87.0 \\ 1 & 1.010 & -32.9 \\ 1 & 0.654 & \Delta H_l \end{vmatrix} \begin{matrix} M \\ P \\ l_1 \end{matrix}}{\begin{vmatrix} 1 & 0 & 1.333 \\ 1 & 1.010 & 0 \\ 1 & 0.654 & 0.388 \end{vmatrix} \begin{matrix} M \\ P \\ l_1 \end{matrix}} \qquad [5]$$

the enthalpy of the oxysulfide at 942°C is $\Delta H_l = -36.4$ kcal per g-atom Fe. A similar value of ΔH_l is obtained from the slope of *i* in Fig. 2. The composition of this liquid is represented by $0.02\ Fe_3O_4 \cdot 0.11\ FeO \cdot 0.32\ FeS$; the enthalpy calculated for an ideal solution is $\Delta H_l = -41.2$ kcal per g-atom Fe which is about 5 kcal more negative than the value obtained from Eq. [5].

Univariant *e* [Iron, Wustite, Liquid (1)]

The equilibrium $p_{S_2} = 4.2 \times 10^{-7}$ atm at 1120°C for univariant *e* is obtained from the data of Bog and Rosenqvist[17] for unit iron activity. The solubility of sulfur in wustite in equilibrium with iron has been measured in the present work (Part II) giving $p_{S_2} = 9.0 \times 10^{-7}$ atm at 1250°C for this univariant.

By approximating the oxysulfide liquid as an ideal solution of FeO and FeS, the sulfur potential for this univariant equilibrium may be estimated using the available free energy data[13]

$$2\,FeS(l) = 2\,Fe(\gamma) + S_2(g);\ \Delta F° = 56{,}680 - 14.96T \qquad [6]$$

together with the composition of the liquid oxysulfide for univariant *e* taken from the phase diagram by Hilty and Crafts,[10] Naldrett,[14] and by Darken and Gurry (Appendix), *e.g.* $N_{FeS} = 0.58$, 0.52 and 0.38 at 1000°, 1100° and 1200°C, respectively.

The experimental and calculated sulfur potentials for this univariant are given in Fig. 3. It is seen that the assumption of ideal behavior in the liquid oxysulfide in equilibrium with iron and wustite, relative to the species liquid FeO and liquid FeS, appears to be a good approximation.

Univariant *f* [Iron, Pyrrhotite, Liquid (1)]

Using $\Delta H_l = -43.5$ kcal per g-atom Fe for the enthalpy of the liquid oxysulfide at 915°C, the slope of the univariant *f* is calculated, giving $d\,RT \ln p_{O_2}/dT = 0.019$ kcal per deg. The curve *f* drawn in Fig. 1 with this slope at 915°C passes through a maximum at a higher temperature, then dips steeply approaching asymptotically to the Fe-S eutectic invariant at 988°C.

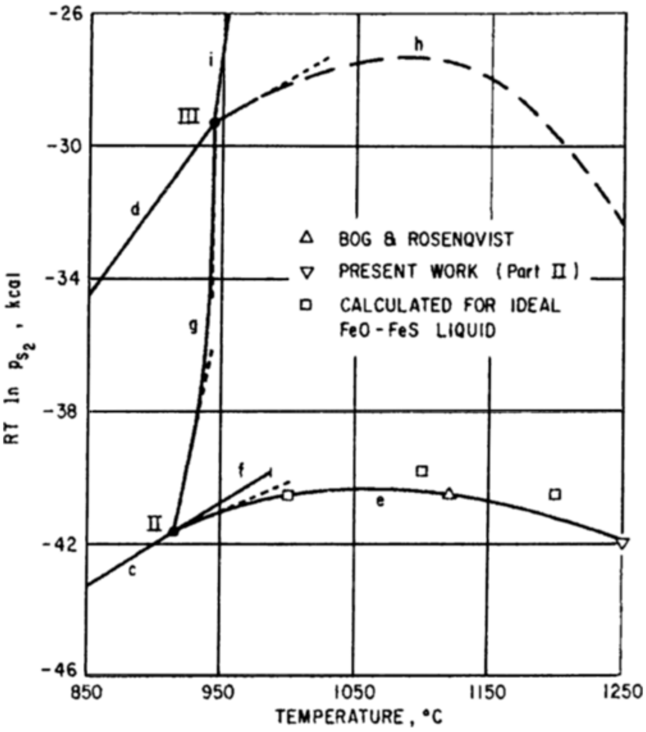

Fig. 3—Construction of univariants, Fe-S-O system. *e*) Iron, wustite, liquid (1); *g*) wustite, pyrrhotite, liquid (1); and *h*) wustite, magnetite, liquid (1).

Univariant *g* [Wustite, Pyrrhotite, Liquid (1)]

The slopes of this univariant for oxygen and sulfur potential diagrams are calculated in the manner demonstrated above using the appropriate enthalpy data in Table II for 915° and 942°C. The values obtained are

°C	$\frac{d\,RT \ln p_{O_2}}{dT}$ kcal per deg	$\frac{d\,RT \ln p_{S_2}}{dT}$ kcal per deg
915	0.28	0.28
942	1.63	1.78

According to the qualitative use of the theorem, the slopes at 942°C for *g* should have been negative. Since the slope is steep, a slight change in the composition of the liquid for this invariant would change the sign of the calculated slope. Because of this uncertainty, the curve *g* in Figs. 1 and 2 is drawn vertical in the vicinity of the invariant temperature 942°C, indicating that the composition of the peritectic liquid is colinear with those of wustite and pyrrhotite.

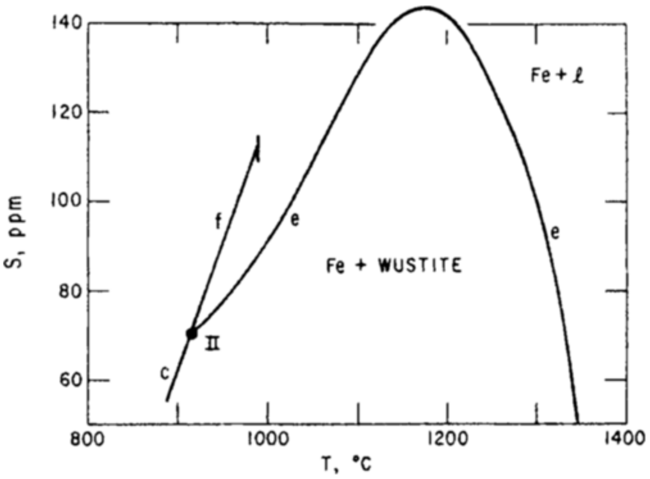

Fig. 4—Sulfur content of iron in equilibrium with wustite and liquid oxysulfide, Fe-S-O system. *c*) Iron, wustite, pyrrhotite; *e*) iron, wustite, liquid (1); *f*) iron, pyrrhotite, liquid (1).

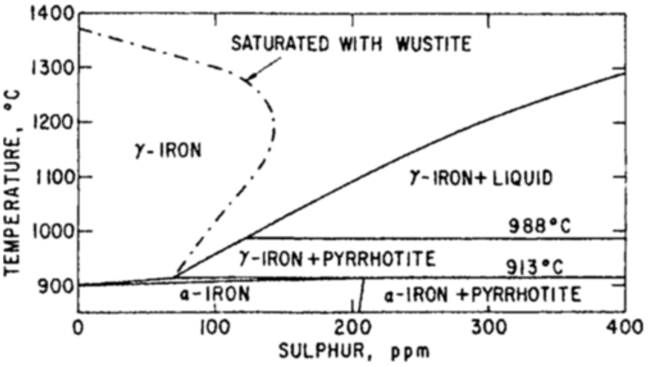

Fig. 5—Sulfur content of γ-Fe corresponding to univariant *e* (Fe-S-O system) superimposed on binary Fe-S phase diagram.

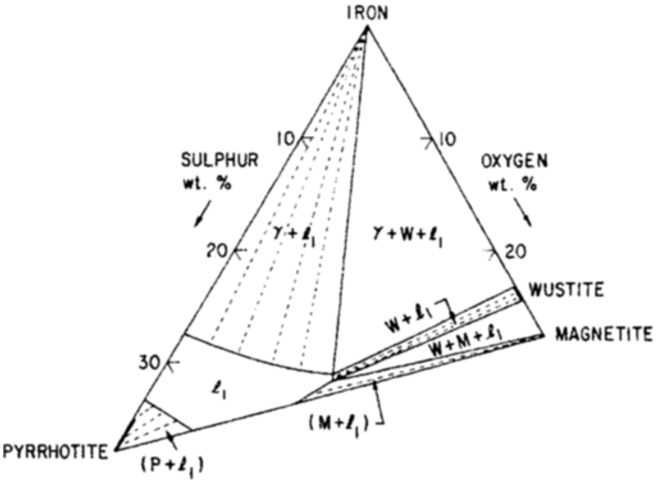

Fig. 6—1100°C isotherm for Fe-S-O system. (γ) gamma iron; (*W*) wustite; (*M*) magnetite; (*P*) pyrrhotite; (l_1) liquid (1).

Univariant *h* [Wustite, Magnetite, Liquid (1)]

The slope of the univariant *h* at 942°C in the sulfur potential diagram is derived from the determinant

$$\frac{d\ln a}{d(1/T)} = \frac{1}{R}\;\frac{\begin{array}{|ccc|l} 1 & 1.13 & -72.09 & W \\ 1 & 1.333 & -87.00 & M \\ 1 & 0.388 & -36.4 & l_1 \end{array}}{\begin{array}{|ccc|l} 1 & 1.13 & 0 & W \\ 1 & 1.333 & 0 & M \\ 1 & 0.388 & 0.654 & l_1 \end{array}} \qquad [7]$$

giving $d \ln a_S/d(1/T) = -29.4/R$ which in turn gives $d\,RT \ln p_{S_2}/dT = 0.024$ kcal per deg. The remainder of this univariant is not known; however, as shown in Figs. 2 and 3 it has to pass through a maximum and then approach the Fe-O invariant 1424°C asymptotically. Assuming ideality for the liquid phase, the curve *h* in Fig. 3 can be calculated in a manner similar to that used for the univariant *e* discussed earlier. The slope of *h* at 942°C thus calculated exceeds that of *d*. That is, the metastable extension of the curve *h* calculated for an ideal liquid oxysulfide lies between *d* and *g* (not shown in Fig. 3). This is in disagreement with the theorem, suggesting that the mole fraction of FeS in this liquid is not equal to its activity. On the other hand, as shown in Fig. 3 liquid oxysulfide for univariant *e* is close to ideal.

Sulfur Solubility in Iron Saturated with Wustite

The solubility of sulfur in γ iron measured by Rosenqvist and Dunicz[18] and by Turkdogan *et al.*[19] gives for the equilibrium constant of the reaction

$$\frac{1}{2}\,S_2(g) = \underline{S}(1 \text{ wt pct in } \gamma\text{-Fe});$$

$$\log \frac{[\%\,S]}{(p_{S_2})^{1/2}} = \frac{2443}{T} - 0.522 \qquad [8]$$

Since the oxygen solubility in iron is small,[20] its effect on the activity coefficient of sulfur is negligible. Therefore, using Eq. [8] the solubility of sulfur in iron saturated with wustite can be computed from the univariant *e* in Fig. 2. Three univariant equilibria in the presence of iron for the invariant point II are shown in Fig. 4. The region below the curves *c* and *e* is the iron + wustite field. The other side of the curve *e* is for iron + liquid (1).

The striking effect of oxygen on the solubility of sulfur in iron (in equilibrium with sulfur containing liquid) is demonstrated in Fig. 5 where the iron/wustite/liquid oxysulfide univariant (dot-dash line) is superimposed on the iron-rich side of the Fe-S phase diagram. At wustite saturation there is a pronounced bulge on the sulfur solubility curve, reaching a maximum of 143 ppm S at 1200°C; this is about one half that corresponding to the solidus of the Fe-S system.

1100° and 1400°C-Isotherms

The isothermal sections can readily be constructed from the available data on phase equilibria in this ternary system. Fig. 6 is for 1100°C showing composition ranges for univariants *e* and *h* (three condensed phases), four two-phase equilibria and one liquid phase. Fig. 7 is for 1400°C showing regions of the miscibility gap univariant and other phase equilibria.

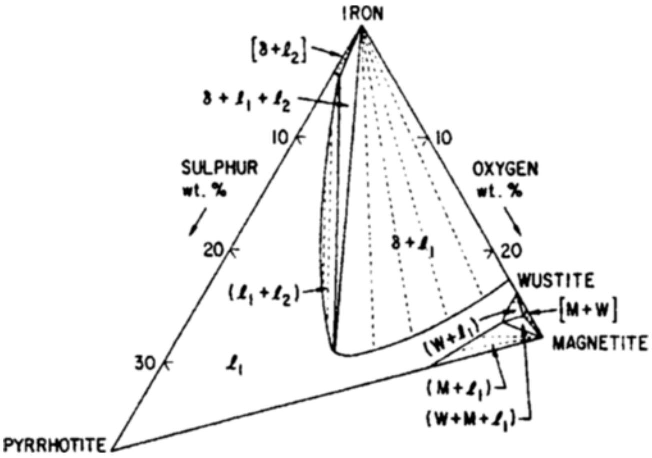

Fig. 7—1400°C isotherm for Fe-S-O system. (δ) delta iron; (*W*) wustite; (*M*) magnetite; (l_1) liquid oxysulfide; (l_2) liquid metal.

OTHER TERNARY SYSTEMS

Information on other ternary systems of the Fe-Mn-S-O quaternary is meager; however, an estimate can be made for some of the invariant equilibria of interest in the present work.

Fe-Mn-O System

There are complete series of liquid and solid solubility in the binary systems Fe-Mn and "FeO"-"MnO" where Raoult's law is essentially obeyed. In contrast to this simplicity, there is an extensive liquid miscibility gap across the metal-metal oxide part of the system from the Fe-O to the Mn-O side. Apart from this semiquantitative information, and investigations done thirty years ago,[21] little else is known about the phase equilibria in the metal-metal oxide part of this ternary system, except of course for the Mn-O deoxidation equilibria in liquid iron. It would seem reasonable to assume that there is only one invariant equilibrium in this part of the system consisting of δ-iron, liquid metal, solid oxide-Fe(Mn)O- and liquid oxide-Fe(Mn)O. The temperature of this ternary invariant is estimated to be ~1527°C which is the invariant temperature for the Fe-O binary system. There are adequate thermodynamic data on i) the free energies of formation of manganous oxide[22] and of solution of oxygen in δ-iron,[23] and ii) the oxide equilibria with liquid Fe-Mn[24] alloys, that an estimate can be made of the equilibrium manganese and oxygen contents of iron for this invariant; calculated data are given in Table III.

Fe-Mn-S System

There is a large liquid miscibility gap extending into the system from the Mn-S invariant at ~1580°C close to the Fe-S side. The estimation of the invariant equilibria in this system has to be based on some work done over thirty years ago.[21,25] In the metal-metal sulfide part of the system, there is a eutectic invariant at ~980°C where the equilibrium condensed phases are: γ-iron, solid Mn(Fe)S, solid "FeS", and liquid Fe(Mn)S. The temperature and composition of this ternary eutectic are close to those of the binary Fe-S system.

Table III. Estimated Data for Invariant Equilibria in Fe-Mn-O, Fe-Mn-S and Mn-S-O Ternary Systems

	Fe-Mn-O ternary system		
~1527°C	δ-iron:	580 ppm Mn	52 ppm O
	Liquid iron:	800 ppm Mn	1130 ppm O
	Solid oxide:	$a_{FeO} = 0.65$	$a_{MnO} = 0.35$
	Liquid oxide:	$a_{FeO} = 0.73$	$a_{MnO} = 0.27$
	Gas:	$p_{O_2} = 1.2 \times 10^{-9}$ atm	
	Fe-Mn-S ternary system		
~980°C	Gamma iron:	15 ppm Mn	83 ppm S
	Solid (Fe) sulfide:	$a_{FeS} \simeq 1$	
	Solid (Mn) sulfide:	$a_{MnS} \simeq 0.37$	
	Liquid sulfide:	~1 wt pct Mn	~30 wt pct S
	Gas:	$p_{S_2} = 1.0 \times 10^{-7}$ atm	
	Mn-S-O ternary system		
~1230°C	Liquid manganese:	Traces of S and O	
	Solid oxide:	$a_{MnO} \simeq 0.98$	
	Solid sulfide:	$a_{MnS} \simeq 0.98$	
	Liquid oxysulfide:	~30% Mn, ~35% S, ~35% O	
	Gas:	$p_{O_2} = 7.6 \times 10^{-20}$ atm, $p_{S_2} = 1.5 \times 10^{-12}$ atm	
~1225°C	Solid manganese:	Traces of S and O	
	Liquid manganese:	Traces of S and O	
	Solid oxide:	$a_{MnO} \simeq 0.98$	
	Solid sulfide:	$a_{MnS} \simeq 0.98$	
	Gas:	$p_{O_2} = 5.8 \times 10^{-20}$ atm, $p_{S_2} = 1.2 \times 10^{-12}$ atm	

In the FeS-MnS pseudobinary section,[25] there is a eutectic invariant at 1180°C where pyrrhotite (with negligible manganese in solution) and Mn(Fe)S solid solution (~75 pct FeS) are in equilibrium with liquid sulfide containing ~5 pct MnS. Using the available information on i) the phase equilibria,[21,25] ii) the free energies of formation of iron and manganese sulfides,[22] and iii) the solubility of sulfur in iron and Fe-Mn alloys,[18,19] the equilibrium manganese and sulfur contents are estimated for the eutectic invariant point, and these are given in Table III.

The liquid miscibility gap in this ternary system at 1600°C was measured by Meyer and Schulte[26] and by Korber.[27] However, as pointed out by Schurmann,[28] there is uncertainty concerning the presence or abscence of a peritectic invariant where the equilibrium condensed phases are: γ-iron, solid Mn(Fe)S, liquid metal, and liquid sulfide. According to Wentrup,[21] there is a peritectic invariant at ~1385°C where two liquids are in equilibrium with solid iron and sulfide phases. On the other hand, Vogel and Hotop[25] show that the miscibility gap univariant terminates at the critical temperature 1370°C (76 pct Fe, 4 pct Mn, and 21 pct S) without intersecting an invariant point. That is, the liquidus dome of the miscibility gap in the composition-temperature diagram terminates on the Mn(Fe)S liquidus surface where there is a univariant equilibrium. Recent investigations done by Bigelow[29] on sulfide inclusions in steel lend support to Vogel's version of this phase diagram, *i.e.* there is no peritectic invariant.

Mn-S-O System

There is a large liquid miscibility gap in this system extending from the Mn-MnO to the Mn-MnS side. The

MnO-MnS pseudobinary side has a eutectic invariant at 1232°C where the mutual solubilities between MnO and MnS are about 2 wt pct.[30] Two invariant equilibria are expected to exist in the metal-oxide-sulfide part of the diagram. The miscibility gap invariant consisting of condensed phases, "MnO", "MnS", liquid oxysulfide, and liquid metal probably exists at ~1230°C. The second invariant equilibrium is estimated to be at ~1225°C where the equilibrium condensed phases are: γ-manganese, liquid manganese, "MnO" and "MnS". Estimated data for these invariants are given in Table III.

Fe-Mn-S-O Quaternary System

Little is known about the phase equilibria in this quaternary system. Wentrup[21] investigated the melting temperatures in "FeO"-MnO-FeS-MnS mixtures about thirty years ago and observed the eutectic temperature to be less than 910°C. In a similar investigation done about ten years ago, Geissler and Kohlmeyer[31] made essentially the same observations and placed the quaternary eutectic at 900°C and gave for the composition of the eutectic liquid 45 mole pct FeO, 40 mole pct FeS and 15 mole pct MnS. In these experiments the melts were contained in alumina or zirconia crucibles and were heated in nitrogen. Under these experimental conditions of unknown manganese, sulfur and oxygen activities, little use can be made of the phase relations proposed by these investigators.

From microscopic examinations of quenched samples, Hilty and Crafts[32] observed the formation of two liquids in the Fe-Mn-S-O quaternary system in equilibrium with solid iron containing 1.0 pct Mn and solid Mn(Fe)O at 1475°C. (This is discussed further later in this section.)

Although available information is meager, it is reasonable to assume that there may be two invariant equilibria in the metal-metal sulfide-metal oxide part of the system: the eutectic invariant and the miscibility gap invariant.

As a rough estimate, the eutectic invariant is assumed to be at 900°C where the equilibrium condensed phases are expected to be: γ-iron, Fe(Mn)O, FeS, Mn(Fe)S and liquid oxysulfide, l_1. Using the phase diagram given by Vogel and Hotop[25] for the FeS-MnS system, the sulfide activities at 900°C are estimated to be $a_{\text{FeS}} \simeq 1$ and $a_{\text{MnS}} \simeq 0.4$, hence the equilibrium manganese content of γ-iron is calculated to be ~10 ppm from the free energy data for the sulfides. Using this manganese concentration, the corresponding equilibrium oxide composition is $N_{\text{MnO}}/N_{\text{FeO}} \simeq 1$. On the basis of these crude estimates, the corresponding equilibrium oxygen and sulfur partial pressures are: 3.8×10^{-18} atm O_2 and 1.4×10^{-8} atm S_2.

The univariant equilibrium of particular importance in practice is that involving four condensed phases, γ-iron, Mn(Fe)O, Mn(Fe)S and liquid (1). An estimate of this univariant can be made on the premise of an ideal liquid oxysulfide solution. The elementary statistical mechanics as applied by Temkin[33] and by Flood *et al.*[34,35] leading to the thermodynamics of ideal fused salt solutions can be used for the present case. That is, the sum of the activities of oxides and sulfides is unity for an ideal liquid oxysulfide solution, thus relative to the pure liquid oxide and sulfide as the standard state,

$$a_{\text{FeO}} + a_{\text{FeS}} + a_{\text{MnO}} + a_{\text{MnS}} = 1 \qquad [9]$$

As shown earlier, the ideal mixing in FeO-FeS liquid in equilibrium with γ-iron and in MnO-MnS is a good approximation. Furthermore, FeO-MnO is known to form an ideal solid and liquid solution. Therefore, the assumption of ideal solution for the quaternary FeO-FeS-MnO-MnS is considered reasonable.

The equilibrium constants of reactions to be considered are taken from the available data[22]

$$\text{MnO}(s) + \text{Fe}(s) = \text{FeO}(l) + \text{Mn}(s);$$

$$\log K_1 = -\frac{8153}{T} + 1.515 \qquad [10]$$

$$\text{MnS}(s) + \text{Fe}(s) = \text{FeS}(l) + \text{Mn}(s);$$

$$\log K_2 = -\frac{8125}{T} + 1.985 \qquad [11]$$

$$\text{MnO}(s) = \text{MnO}(l);\ \log K_3 = -\frac{2842}{T} + 1.379 \qquad [12]$$

$$\text{MnS}(s) = \text{MnS}(l);\ \log K_4 = -\frac{1377}{T} + 0.765 \qquad [13]$$

where (s) is solid and (l) is liquid.

At manganese activities (= atom fraction in iron, N_{Mn}) corresponding to about 1 or 2 pct, the iron content of solid manganese oxide and sulfide is sufficiently low that their activities are approximated as unity, *i.e.* $a_{\text{MnS}} \simeq 1$ and $a_{\text{MnO}} \simeq 1$. With these simplifications, an expression is obtained for the equilibrium manganese content of solid iron for this univariant.

$$(K_1 + K_2)\,\frac{1 - N_{\text{Mn}}}{N_{\text{Mn}}} + K_3 + K_4 = 1 \qquad [14]$$

The manganese of the metal thus computed for this univariant is shown by the dotted curve in Fig. 8. As discussed earlier, $a_{\text{MnS}} \simeq 0.4$ and $a_{\text{MnO}} \simeq 0.5$ at the invariant temperature 900°C. With increasing temperature and manganese content along this univariant, the activities of manganous sulfide and oxide increase. Since a_{MnS} as a function of composition is not known, the curve j in Fig. 8 is an estimate for this univariant starting at 10 ppm Mn at 900°C for $a_{\text{MnS}} = 0.4$ and $a_{\text{MnO}} = 0.5$, and blending into the dotted curve at ~1 pct Mn for which a_{MnO} and $a_{\text{MnS}} \to 1$ is a good approximation.

There is limited solubility of pyrrhotite in MnS; assuming that Raoult's law is obeyed, the manganese content of γ-iron in equilibrium with solid Mn(Fe)S and liquid sulfide may be estimated using the available phase diagram for the system "FeS"-"MnS". This univariant equilibrium for the ternary system Fe-Mn-S is shown in Fig. 8; there is a temperature maximum at ~1500°C, and the univariant k terminates at the Mn-S invariant 1230°C.

The curves j and k in Fig. 8 reveal the significant effect of oxygen in lowering the melting point of the oxysulfide phase. For example, at 1200°C no liquid phase forms in the Fe-Mn-S system, if there is more than 0.01 pct Mn in the iron. On the other hand, when iron is saturated with "MnO" and "MnS", the manganese content of the metal must exceed 1 pct to suppress the formation of the liquid oxysulfide at 1200°C.

On the basis of the information cited above (partly

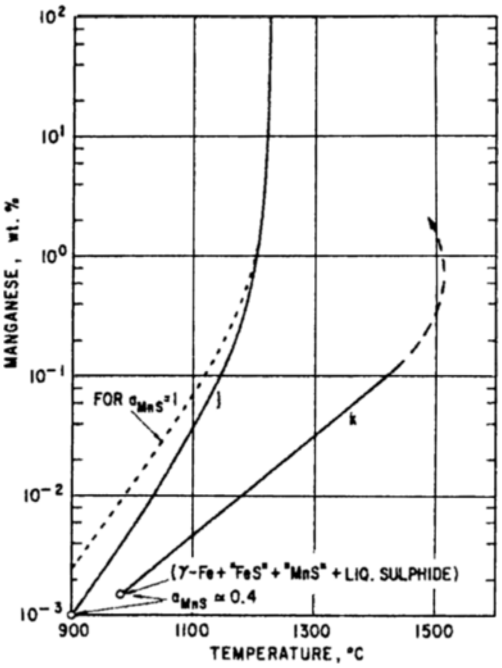

Fig. 8—Manganese content of the metal for univariant equilibrium γ-Fe + "MnO" + "MnS" + liquid (l) for Fe-Mn-S-O system and univariant equilibrium γ-Fe + "MnS" + liquid sulfide for Fe-Mn-S system.

experimental and partly estimated), the manganese potential diagram is constructed, at least approximately, in Fig. 9 for two invariant equilibria involving the presence of metal and oxide phases. The univariant *n* [γ-iron, wustite, pyrrhotite, liquid (1)] approaches the invariant 915°C asymptotically for the Fe-S-O ternary system. Because of the low MnO solubility product, in iron containing more than about 1 pct Mn, the amount of oxygen in solution is small and has negligible effect on the Fe-Mn solidus temperature. Therefore, the univariant *q* [solid iron, "MnO", liquid oxysulfide (l_1), liquid metal (l_2)] starting from the invariant 1527°C for the Fe-Mn-O system follows closely the solidus curve of the Fe-Mn system and intersects the univariant *j* at about 90 pct Mn and slightly below the estimated eutectic temperature, ~1225°C, of the Mn-S-O system. The liquid miscibility gap observed by Hilty and Crafts[32] at 1475°C with δ-iron containing 1 pct Mn cannot be the equilibrium value. Because of slow manganese diffusion in solid iron, the melt was apparently not in equilibrium with the container made of Fe-1 pct Mn alloy. For this univariant the estimated manganese content in solid iron is about 12 pct at 1475°C. Although the positions of the curves in Fig. 9 are not known accurately, they demonstrate the conceptually correct form of representing the univariant equilibria in the quaternary system.

Estimated data for two invariants in the Fe-Mn-S-O quaternary system are given in Table IV.

GENERAL REMARKS

In an attempt to understand one of the possible causes of hot-shortness in low-alloy steels, we should take a closer look at the phase equilibria in the appropriate part of the Fe-Mn-S-O system. Because of the low solubility of oxygen in iron, all commercial steels contain oxides. Assuming that all other alloying elements are absent, a Mn(Fe)O oxide will be present at all temperatures of interest, for which relevant data are given in Fig. 9.

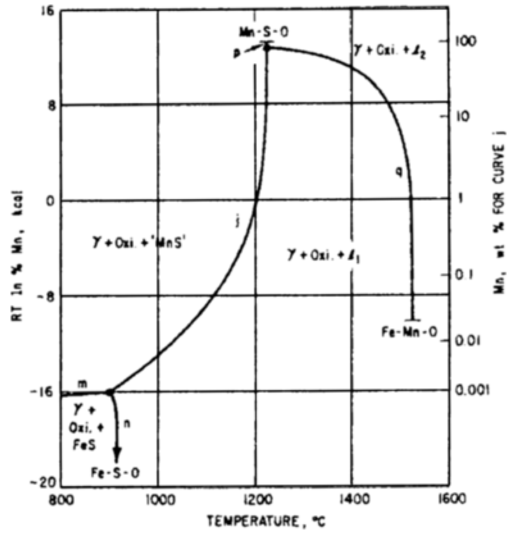

Fig. 9—Univariant equilibria in Fe-Mn-S-O system in the presence of γ-Fe and Mn(Fe)O phases. *j*) Fe, Oxi., "MnS", l_1; *m*) Fe, Oxi., "MnS", "FeS"; *n*) Fe, Oxi.. "FeS", l_1; *p*) Fe, Oxi., "MnS", l_2; and *q*) Fe, Oxi., l_1, l_2.

Table IV. Estimated Data for Invariant Equilibria in Fe-Mn-S-O Quaternary System

~900°C	γ-iron	~10 ppm Mn	< 1 ppm 0
	Solid (Mn) sulfide:	$a_{MnS} \simeq 0.4$	
	Solid (Fe) sulfide:	$a_{FeS} \simeq 1$	
	Fe(Mn)O oxide:	$a_{MnO} \simeq 0.5$	$a_{FeO} \simeq 0.5$
	Liquid (1) oxysulfide:	~26 pct FeO, 54 pct FeS, 15 pct MnS and 5 pct MnO by weight	
	Gas:	$p_{O_2} \cong 3.8 \times 10^{-18}$ atm, $p_{S_2} \cong 1.4 \times 10^{-8}$ atm	
~1225°C	Solid Fe/Mn:	~90 pct Mn	
	"MnS":	$a_{MnS} \simeq 1$	
	"MnO":	$a_{MnO} \simeq 1$	
	Liquid (1):	~0.1 pct FeO, 0.3 pct FeS, 65.2 pct MnS and 34.4 pct MnO by weight	
	Liquid (2):	(pct O/pct S) for l_2 (metallic) <(pct O/pct S) for l_1 (oxysulfide)	

At the eutectic, 900°C, invariant the estimated manganese in solution in iron is about 10 ppm. However, along the univariants *j* and *p* the equilibrium manganese content increases steeply with increasing temperature until at ~1225°C the univariant *p* terminates on the Mn-S-O plane for which the γ phase is essentially 100 pct Mn. It is evident that as long as the steel contains Mn(Fe)O and Mn(Fe)S in equilibrium with the metal, a liquid oxysulfide may form somewhere between 900° and 1225°C, depending on the concentration of manganese in solution in steel. There are, of course, well-known and practiced remedies which will inhibit the formation of a liquid phase in steel at hot-working temperatures.

If most of the oxygen in steel is tied up as "inert" oxides, *e.g.* TiO_2, ZrO_2, Al_2O_3,* a small amount of manganese would be adequate to suppress the formation of a liquid sulfide phase, as evidenced from the

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*If there is excess aluminum in solution, Al_2S_3 may also form; this sulfide melts at 1100°C, therefore, its presence in steel may not be desirable.

MnS solubility data of Turkdogan *et al.*[19] and from comparison of univariants j and k in Fig. 8 for Fe-Mn-S-O and Fe-Mn-S systems, respectively.

Another remedy is to lower the sulfur content of steel. For example, as pointed out earlier, Fig. 5, in the case of a simple Fe-S-O system, no liquid oxysulfide should form when the steel contains less than 70 ppm S, despite the presence of iron oxide. This argument is valid only when no manganese is present in the metal. What is, of course, more effective is to tie up sulfur as a stable sulfide. In fact, it has long been known[36,37] that the addition of rare earth elements, *e.g.* cerium and lanthanum, to stainless steel where the oxygen content is low improves the hot workability.

Although the formation of a low-melting oxysulfide at hot-working temperatures can readily be inhibited by the appropriate addition of alloying elements and by the control of sulfur and oxygen contents (already done in practice), subsequent scaling of slabs or ingots during heating can alter this situation and may become responsible for the formation of a liquid oxysulfide. When an iron-oxide scale forms, some manganese is oxidized and the concentration of manganese in solution near the iron-wustite interface decreases. That is, if the initial composition of steel were somewhere above the curve j in Fig. 9, upon scale formation it could be shifted below the curve into another three-phase region where a liquid phase appears.

Another important consequence of scaling is the enrichment of sulfur in solution in iron. Because of the relatively low sulfur solubility and diffusivity in iron and wustite, the oxidation of iron may result in sulfur accumulation at the interface, ultimately leading to the formation of a liquid oxysulfide. This is indeed analogous to the precipitation of copper or tin at the metal-oxide interface during the oxidation of iron alloys observed by many investigators.[38] In fact, Buchholtz and Pusch[39] did observe the precipitation of an oxysulfide at the iron-wustite interface; however, these investigators did not give an explanation of their observation. Kiessling and Lange also report[40] the precipitation of a liquid oxysulfide along grain boundaries near the iron-wustite interface when the steel is heated under oxidizing conditions in furnaces fired with sulfur-containing fuel oil.

In Part II of this paper, the results of experimental work are given, demonstrating the formation of pyrrhotite or oxysulfide liquid during the oxidation of Fe-Mn alloys containing sulfur.

CONCLUSIONS

By applying Darken's modification of the Morey-Williamson theorem on univariant curves intersecting at an invariant point, the enthalpy of formation of liquid oxysulfide is estimated for the Fe-S-O system, *e.g.* −43.5 kcal per g-atom Fe at the eutectic invariant 915°C and −36.4 kcal per g-atom Fe at the peritectic invariant 942°C. The univariant curves for condensed phases iron-wustite-liquid (1) and wustite-magnetite-liquid (1) in the sulfur potential diagram for the Fe-S-O system pass through maxima at ~1050° and ~1100°C.

The univariant curve for wustite-pyrrhotite-liquid (1) equilibrium in the Fe-S-O system has steep slopes, $d\,RT \ln p_{S_2}/dT$ and $d\,RT \ln p_{O_2}/dT$, in the vicinity of the peritectic invariant 942°C. This finding suggests that the compositions of these three condensed phases are nearly colinear in the composition diagram normally used.

The solubility of sulfur in γ-iron decreases with increasing oxygen content. The sulfur content of iron in equilibrium with wustite and liquid oxysulfide reaches a maximum of 143 ppm at 1200°C; this is about one half of that in purified iron. At the eutectic invariant (915°C), the sulfur in solution in equilibrium with wustite and liquid (1) is 70 ppm. The sulfur solubility in γ-iron saturated with wustite decreases with increasing temperature above 1200°C. That is, for sulfur contents between 70 and 143 ppm in wustite-saturated iron (no alloying elements being present), liquid oxysulfide may be absent over a temperature range, which depends on the sulfur content.

In the quaternary system Fe-Mn-S-O involving the γ-phase, there are two invariant points: the eutectic invariant at 900°C with ~10 ppm Mn in γ-iron and the miscibility gap invariant at ~1225°C where the equilibrium manganese content of iron is estimated to be ~90 pct. The equilibrium manganese content of iron for the univariant γ-iron-Mn(Fe)O-liquid (1)-liquid (2) decreases with increasing temperature, *e.g.* ~12 pct Mn at 1475°C and ~0.06 pct Mn at the ~1527°C invariant of the Fe-Mn-O system.

The univariant equilibrium of practical importance is that involving the condensed phases γ-iron, Mn(Fe)O, Mn(Fe)S, and liquid oxysulfide. It is found that as long as the steel contains Mn(Fe)O and Mn(Fe)S in equilibrium with the metal, a liquid oxysulfide may form somewhere between 900° and 1225°C, depending on the concentration of manganese in solution in steel (in the absence of other alloying elements), *e.g.* for 10 ppm Mn, 900°C and for ~90 pct Mn, ~1225°C. In the absence of oxygen, however, a very small amount of manganese (*e.g.* 20 ppm Mn at 1000°C and 400 ppm at ~1300°C) is sufficient to suppress the formation of the liquid sulfide.

Because of the relatively low sulfur solubility and diffusivity in iron and wustite, the present analysis of the equilibrium suggests that the oxidation of an Fe-Mn-S alloy may result in sulfur accumulation at the interface, ultimately leading to the formation of a liquid oxysulfide. This is demonstrated in the experimental work presented in Part II.

ACKNOWLEDGMENT

The authors are indebted to L. S. Darken for his counsel in the progress of this work and for the use of his unpublished work concerning further developments of the Morey-Williamson theorem.

Appendix

Melting Temperatures of Wustite-Pyrrhotite Mixtures

L. S. DARKEN AND R. W. GURRY

About thirty years ago, we investigated the liquidus temperatures of that portion of the Fe-S-O system in

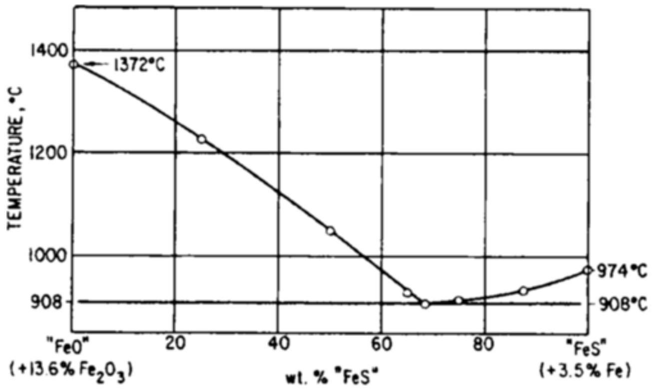

Fig. A1—Melting diagram of system iron oxide—iron sulfide in equilibrium with metallic iron.

equilibrium with metallic iron. Because of current interest, the results of this early work (previously unpublished) are given here.

The melts were all made in an iron crucible ($\frac{1}{4}$ in. ID, $\frac{3}{4}$ in. long). The charge consisted of a mixture of pyrrhotite and wustite. The pyrrhotite used contained 35.1 pct S and 64.9 pct Fe, close to the stoichiometric composition (36.5 pct S) but with about 3.5 pct excess of Fe. The wustite used was prepared by reaction of high-purity hematite with iron in an iron crucible; it analyzed 76.8 pct Fe, 23.2 pct O, or 86.4 pct FeO, 13.6 pct Fe_2O_3. The selected mixture was made by weighing the powdered sulfide and oxide (200 mesh) and placing the iron crucible, which was then pinched closed and held at temperature in a precision-controlled platinum wire-wound furnace; the atmosphere used was purified nitrogen. After holding at temperature for 20 to 40 min, the sample was quenched in mercury. It was then sectioned and polished for examination under a metallographic microscope. Fifty-five melts were prepared of eight different compositions, which corresponded to wustite, pyrrhotite and mixtures with wustite containing 25, 50, 65, 68.5, 75, and 87.5 pct pyrrhotite. From the structural details of the polished samples examined microscopically, it was possible to identify the phase region from which the equilibrated sample was quenched, *e.g.* above or below the liquidus. By quenching a number of samples of a given mixture from several closely spaced temperatures, it was possible to evaluate the liquidus temperature.

The temperatures so obtained are given in Fig. A1 showing the liquidus curves and the eutectic invariant of wustite-pyrrhotite mixtures in equilibrium with iron. Since the wustite-pyrrhotite join is not a pseudobinary section, the compostiion of the melt in equilibrium with iron will change with temperature. Hence, the percentages on the abscissa are not the percentages of FeS and FeO, but indicate the relative proportions of "iron sulfide" (35.1 pct S) and wustite (23.2 pct O) used in making up the mixtures. The liquidus curve is the intersection of the liquidus surfaces in the Fe-S-O ternary system for the γ-iron/liquid and wustite/liquid to the left of the eutectic point in Fig. A1; to the right of the eutectic point, it is the intersection of the γ-iron/liquid and pyrrhotite/liquid liquidus surfaces.

As discussed in the paper, the temperature of the eutectic invariant, 908°C, obtained in this work is in reasonable accord with the results of subsequent work by other investigators.

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