

The Solubility of the Liquid Oxysulfide Phase in Liquid Fe-O-S Alloys

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The solubility of the liquid oxide phase in liquid Fe-O alloys has been measured for the temperature range of 1378 to 1740 °C. Also the solubility of the liquid oxysulfide phase in liquid Fe-O-S alloys has been determined for the composition range of 0.08 to 0.30 wt pct oxygen and 0 to 0.5 wt pct sulfur. The oxygen content of liquid iron saturated with the liquid oxide phase is $\log O = -6358/T + 2.76$. The standard free energy for the formation of the oxide phase is: $x\text{Fe}(l) + \text{O}(\text{pct}) = \text{Fe}_x\text{O}(l)$; $\Delta G^\circ = 242.4 - 0.0829T + 166,990/T$ (kJ). The equation for the standard free energy in the temperature range of 1550 to 1650 °C may be written as: $-117.5 + 0.0496T$ (kJ). The effect of composition on temperature of saturation of liquid Fe-O-S alloys with the oxysulfide phase is: $T(\text{K}) = -6358/(\log \text{pct O} - 2.76) - (\text{pct S}) \times [554 + 135.0(\log O - 2.77)]$. The relationship applies for the composition range of 0.15 to 0.30 wt pct oxygen and 0.0 to 0.5 wt pct sulfur and temperatures from 1480 to 1680 °C.

I. INTRODUCTION

THE solubility of "FeO" and of the iron-oxysulfide in liquid iron has been measured by a novel method employing levitation melting. The method was selected because it avoided the need for a crucible to contain the melt, which in turn avoided possible contamination of the nonmetallic phase with the crucible material and possible loss of sulfur and oxygen to the crucible from the iron melt. In addition, electromagnetic stirring assured complete mixing of the liquid. A small pellet of iron that contained specified concentrations of oxygen and sulfur was levitated and melted in a stream of argon, and then brought to a high temperature where these nonmetallic elements were completely dissolved in the liquid iron. The specimen was then cooled slowly, and its temperature was monitored. At some temperature, the liquid became saturated with respect to the nonmetallic phase, and a bright fleck of the oxide, or oxysulfide, phase appeared. The temperature at which this occurred was the saturation temperature for the initial composition of the alloy.

The method was particularly interesting because it permitted the melts being studied to be undercooled up to 150 °C below the monotectic temperature in the Fe-O system (1528 °C). Thus, it was possible to study the behavior of the melts over a range of 360 °C.

II. EXPERIMENTAL

The apparatus employed was the levitation system described by Yarwood, Flemings, and Elliott.¹ When levitated, the metal pellet is suspended within a vertical Vycor tube; the levitation coil is positioned outside around this tube. The upper end of the tube is closed with an optical-quality sight glass on which is positioned a glass prism

through which a two-color pyrometer (Milltron) can be sighted down on the upper portion of the levitated specimen. The stream of purified argon passes into this tube through a side tubulation and then flows down past the specimen. A sealed brass box that is attached to the lower end of the Vycor tube contains a turntable. Mounted on the turntable are five boron nitride cups to hold specimens to be levitated and five split copper cups into which the melted specimens can be dropped and quenched. A retractable lifting device that projects through the bottom of the box is utilized to lift a specimen and cup from the turntable and to place the specimen at the center of the levitation coil. The boron nitride cup is then retracted to the turntable once the specimen is levitated.

A. Preparation of Materials

The metal specimens for levitation were small samples (1.5 to 2 gm) of iron which were prepared from 0.5-inch diameter rod stock (Ferrovac-E) by swaging the rod to a diameter of 5 mm. The composition of the iron is shown in Table I. A hole 2 mm in diameter was bored axially into an end and halfway through each specimen. A cylindrical rod of the same diameter as the hole was also machined from the Ferrovac-E stock. A short length of this rod was used to plug the hole in the specimen after preweighed amounts of iron oxide and iron sulfide had been placed in the hole. The

Table I. Compositions of Materials Employed

Material	Composition
Iron; Ferrovac-E	ppm; C-80, Mn-10, P-20, S-50, Si-50, Ni-250, Cr-10, V-40, W-100, Mo-10, Co-40, Cu-10, Sn-20, Pb-5, Al-100, Ni-1.5, N-1.5, O-100, H-0.6
Fe ₂ O ₃ ; Baker and Adamson, Reagent grade	99.5 pct Fe ₂ O ₃
FeS; Reagent grade iron filings and sulfur	S-99.999 pct pure; FeS-64 pct Fe, 35 pct S, 1 pct O

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pieces of iron were filed smooth, pickled in dilute HCl, washed in distilled water, dried in acetone, and stored in a desiccator for use later.

To obtain levitation samples of the desired composition, preweighed quantities of Fe₂O₃ and iron sulfide, if used, were tamped into the hole of a prepared specimen. The hole was then closed by forcing a short piece of the 2 mm diameter rod into place. The exposed end of the rod was then peened over to seal the hole tightly.

The iron sulfide utilized in this study was prepared by placing a preweighed quantity of pure sulfur at the closed end of a quartz tube. The iron powder was placed several cm within the open end of the tube. This tube was then evacuated and sealed. Subsequently the end of the tube containing the iron powder was placed just within the end of a horizontal tube furnace that was held at 950 °C. Over a period of a few hours, the tube was slowly slid into the furnace. Then the tube was withdrawn rapidly and quenched in a bath of ice and water. The analysis of the product is shown in Table I.

The cooling gas was argon which was supplied from steel tanks. To purify the gas, it was passed successively through copper turnings at 450 °C, and then columns of ascarite and phosphorous pentoxide.

B. Temperature Measurement

The temperature of a specimen was monitored by the two-color pyrometer. The pyrometer, optical system, and recorder were calibrated for each set of measurements by observation of the melting point (1536 °C) of a levitated Ferrovac-E specimen. The gas passing downward past the specimen avoided the problem of iron fume obscuring the view of the pyrometer. The output of the pyrometer was plotted on a recording potentiometer. It is estimated that the uncertainty in the temperature measurement was ±3 °C.

C. Experimental Procedure

Five samples and five clean split casting cups were placed on the turntable. The box and levitation system were evacuated by a roughing vacuum pump. The system was then filled with argon and the flow of gas started. The first sample of pure iron was levitated and brought to its melting point to calibrate the temperature measuring system. With care, a sample could be held in the partially liquid state for a short time. The temperature of the sample was raised to above the melting point. The specimen was then solidified and remelted. Finally, the specimen was cast into a copper cup. The rate of change of temperature of the specimen was controlled by regulating the flow rate of the argon stream. It was not possible to determine the equilibrium freezing point of iron because the specimen always undercooled severely.

The alloy (Fe-O and Fe-O-S) samples were then processed. A specimen was levitated, and it was brought to the solution temperature at 1650 to 1700 °C, or to at least 50 °C above the saturation temperature, and homogenized for two minutes. The flow rate of the argon stream was gradually increased and the levitation power was held constant. The temperature of the specimen was reduced slowly until the first bright fleck of the nonmetallic phase appeared. Immediately, the specimen was brought to the solution tempera-

ture, held there for two minutes and recooled to determine the temperature of saturation again. The specimen was reheated to the solution temperature again, held for two minutes, and quenched in a copper cup. If the two saturation temperatures did not agree within 5 °C, the heating and cooling cycle was repeated again. The heating and cooling cycles were kept as short as possible to minimize volatilization from the specimen. The rate of cooling ranged from 5 to 20 °C per minute, and the measured saturation temperature was not affected by the rate.

A number of cast samples was cut up for chemical analysis and metallographic examination. Others were sectioned into three parts and all parts were examined metallographically, or were analyzed chemically. The purpose of this procedure was to check for segregation of oxygen and sulfur in the cast specimen and none was apparent. The analysis for sulfur was by combustion, and for oxygen it was by gas extraction.

Two sets of experiments were performed. The first was with Fe-O alloys in which the oxygen concentration ranged from 0.05 to 0.40 wt pct. The second was with Fe-O-S alloys in which the composition range was 0.15 to 0.30 wt pct oxygen and 0.05 to 0.5 wt pct sulfur.

III. RESULTS

The comparison between the analysis of the specimens as prepared and from the chemical analysis of the half of the quenched specimens is shown in Table II. Two points are of importance: (a) considering the uncertainties in the analytical method and those possible in preparing the specimens, the agreement in the two sets of numbers is excellent; (b) the agreement also shows that the shift in composition of the specimens due to volatilization of components during levitation is small enough to be ignored in this study. As a consequence of these results, the analyses of the specimens as prepared were used in correlations.

The data from the measurements on the Fe-O system are plotted in Figure 1. A least-squares line through the data points gives the equation:

$$\log \text{pct O} = -6358/T + 2.76 \quad [1]$$

for saturation with the Fe_xO(l) phase. This equation with results of other earlier investigations of this same system are

Table II. Compositions of Liquid Specimens

Sample No.	As Made Up, Wt Pct		By Chemical Analysis, Wt Pct*	
	O	S	O	S
F-O-53	0.35	—	0.33	0.002
F-O-54	0.325	—	0.32	0.003
F-O-57	0.1625	—	0.18	0.001
F-O-S-52	0.20	0.15	0.19	0.15
F-O-S-65	0.25	0.25	0.25	0.23
F-O-S-61	0.25	0.10	0.26	0.10
F-O-S-73	0.30	0.20	0.32	0.17
F-O-S-76	0.30	0.15	0.29	0.14
F-O-S-82	0.15	0.15	0.15	0.14
F-O-S-86	0.15	0.30	0.15	0.28
F-O-S-92	0.175	0.15	0.17	0.15

*After experiment, 1/2 of quenched sample.

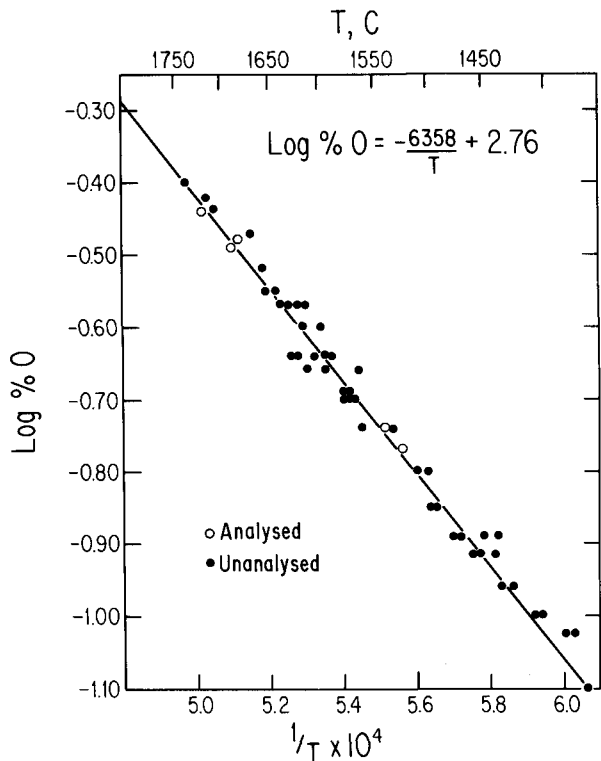


Fig. 1—Concentration of oxygen in liquid iron for saturation with liquid oxide (Fe_xO).

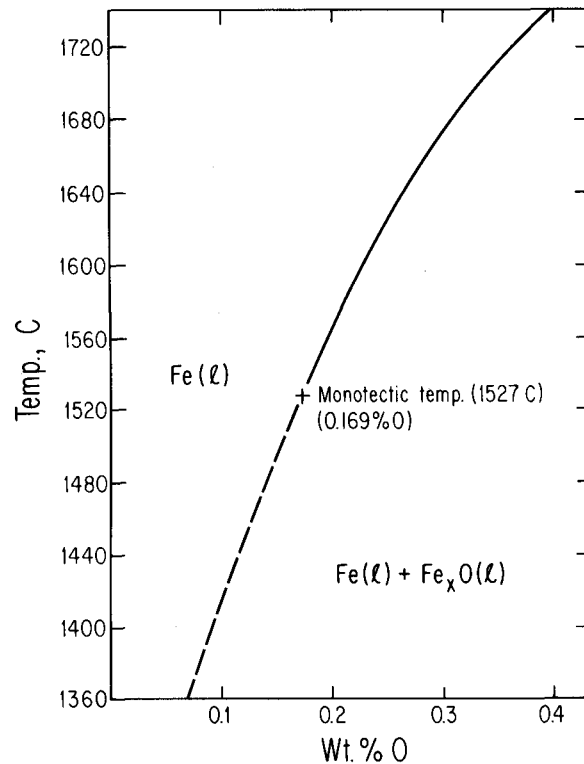
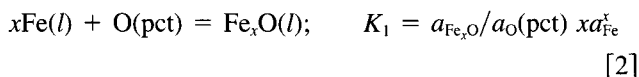


Fig. 2—Liquidus curve for $\text{Fe}(l)\text{-Fe}_x\text{O}(l)$ equilibrium. Dashed portion of line shows conditions for which $\text{Fe}(l)$ is metastable.

shown in Table III. The standard deviation for log pct O is ± 0.006 , and it is ± 47 and ± 0.004 , respectively, for the following two terms in Eq. [1].

The curve of the solubility of the liquid oxide phase in liquid iron for the Fe-O phase diagram based on our results is shown in Figure 2. The pertinent reaction is:



The pct in parentheses shows that the composition coordinate employed is wt pct. Because of undercooling of liquid iron in the measurements, the portion of the line below the monotectic temperature (1527 °C) represents a metastable condition of liquid iron rather than solid iron in the equilibrium.

Measurements for the Fe-O-S system are shown in Figure 3. The lines are fitted by the least-squares method to the data points.

Table III. Solubility of "FeO" in Liquid Iron

Investigation	Temp. Range, C	Log O	Ref.
This study	1378 to 1740	$-6358/T + 2.76$	—
Taylor and Chipman	1520 to 1700	$-6320/T + 2.73$	2
Yarwood <i>et al.</i>	1370 to 1750	$-5750/T + 2.43$	3
Gokcen	1530 to 1700	$-5750/T + 2.43$	4
Fischer and vom Ende	1535 to 1700	$-5762/T + 2.439$	5

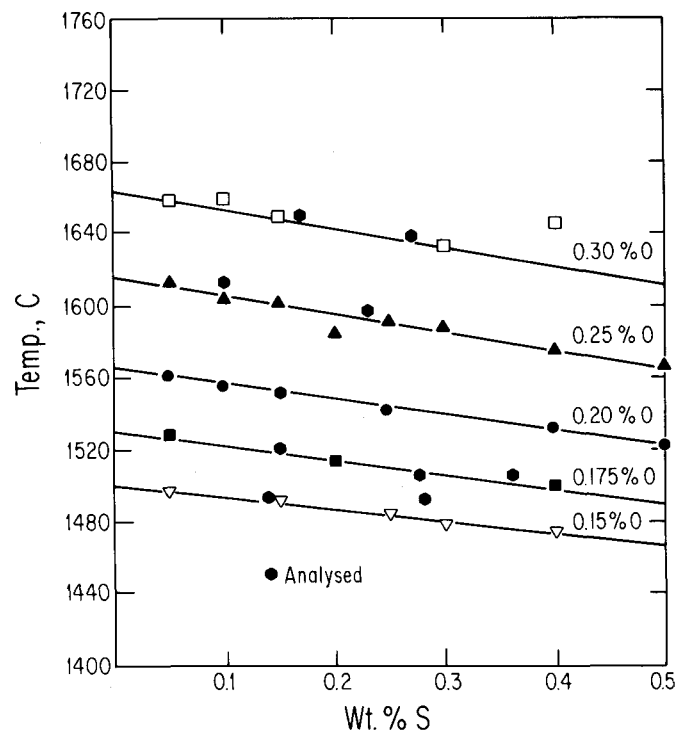


Fig. 3—Iso-oxygen lines on surface of liquid iron saturated with oxy-sulfide.

IV. DISCUSSION

A slightly better correlation of the data is possible by writing the equilibrium constant for Eq. [2] as

$$K_1 = a_{\text{Fe}_2\text{O}}/a_{\text{O}}(\text{pct}) x a_{\text{Fe}}^x \approx 1/[f_{\text{O}}(\text{pct}) \times \text{pct O}] \quad [3]$$

where the activities of the oxide phase and iron are assumed to be unity, and the activity and activity coefficient are based on the infinitely dilute solution of oxygen in liquid iron as the reference state. The activity coefficient of oxygen in iron can be expressed as

$$\log f_{\text{O}}(\text{pct}) = e_{\text{O}}^0 \times \text{pct O} \quad [4]$$

where e_{O}^0 is the self interaction coefficient of oxygen in liquid iron. If the value of the interaction coefficient of $-1750/T + 0.734$ as selected by Sigworth and Elliott⁶ is employed in Eq. [4] and then the data are correlated in terms of $\log a_{\text{O}}$ and $1/T$, the least-squares line through the data points was found to be

$$\log a_{\text{O}}(\text{pct}) = -4.331 + 1.2661 \times 10^4/T - 0.0611 \times 10^8/T^2 \quad [5]$$

By the use of Eq. [5], the standard free energy of formation for Eq. [2] is

$$\Delta G_2^\circ = 242.4 - 0.0829T - 116,990/T \text{ (kJ)} \quad [6]$$

This relationship applies for the temperature range of 1378 to 1740 °C. In the range of 1550 to 1650 °C, the equation may be written as follows:

$$\Delta G_2^\circ = -117,500 + 49.6T \text{ (kJ)} \quad [7]$$

This relationship is in reasonable agreement with that obtained by Taylor and Chipman² which is $\Delta G_2^\circ = -107,500 - 44.27T$. It is to be noted that the terms in the relationship will be influenced somewhat by the value of e_{O}^0 chosen for the calculation. The standard deviation for ΔG_2° (Eq. [2]) is ± 0.2 kJ at 1600 °C, and it is ± 0.9 kJ for ΔH_2° . The results of this study for the Fe-O system agree well with those of previous workers as shown in Figure 4, particularly those of Taylor and Chipman² and Gokcen.⁴ The larger temperature range for this work is to be noted.

The addition of sulfur to the liquid iron narrows the miscibility gap in the Fe-O binary (Figure 3). The following interpolation formula has been developed to describe the temperature for saturation of the liquid iron phase as a function of the concentrations of sulfur and oxygen in the liquid iron:

$$T(\text{K, sat}) = -6358/(\log \text{pct O} - 2.76) + \text{pct S} \\ [-554 - 135(\log \text{pct O} - 2.76)] \quad [8]$$

This equation applies in the range of composition of liquid iron of 0 to 0.5 wt pct sulfur and 0.08 to 0.30 wt pct oxygen and from 1480 to 1680 °C.

The nature of the experiment precluded determination of the composition of the equilibrium oxysulfide phase with which the liquid metal was saturated. On the other hand, it is possible to estimate the concentration of FeS in the phase. This was accomplished by calculating the activity of FeS in the phase employing the reaction

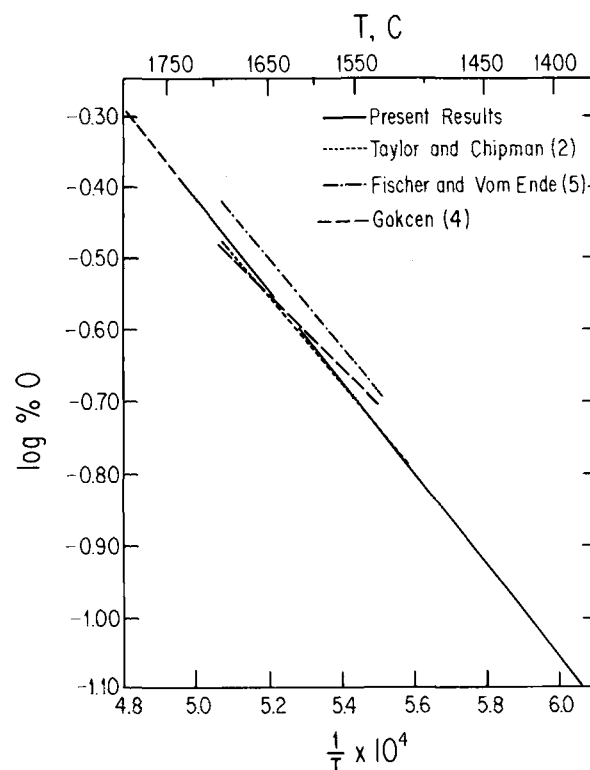


Fig. 4—Comparison of measurements of concentration of oxygen in Fe(*l*) for saturation with Fe₂O(*l*).

The calculation involved the use of the standard free energy formation of FeS (*l*) and of S (pct) from S₂ (*g*),⁷ and the appropriate interaction coefficients for sulfur in liquid Fe-O-S alloys.⁶ It was necessary to assume that the activity of iron was unity, that the oxysulfide phase lies along the binary Fe_{0.95}O-FeS system, and that the activity coefficient of FeS in the oxysulfide phase is 1.5 (Raoultian base). This latter value is based on the measurements of Dewing and Richardson.⁸ The data employed and concentration of FeS in the oxysulfide for several compositions of the liquid metal phase taken from Figure 3 are shown in Table IV. For alloys containing 0.5 wt pct sulfur, the activity of FeS in the non-metallic phase is approximately 0.07 and the concentration is 6 wt pct. The weight ratio of sulfur in the oxysulfide

Table IV. Estimation of the Composition of the Liquid Fe_{0.95}O-FeS Phase in Equilibrium with Fe-O-S Melts (Data from Figure 3)

Temp. C	Metal		Fe _{0.95} O-FeS Liq.	
	Pct S	Pct O	a_{FeS}	Wt Pct FeS*
1500	0.25	0.168	0.0360	3.1
1500	0.25	0.205	0.0359	3.1
1600	0.25	0.260	0.0353	3.0
1650	0.25	0.315	0.0346	2.9
1500	0.50	0.184	0.0705	6.1
1550	0.50	0.220	0.0700	6.0
1600	0.50	0.283	0.0682	5.8
1650	0.50	0.342	0.0665	5.7

* $\Delta G_f^\circ(\text{FeS}) = +9,670 + 9.62T$ (Eq. [9], Refs. 6 and 7)

$e_{\text{S}}^0 = 223/T - 0.153$, $e_{\text{O}}^0 = -0.27$, (6)

$a_{\text{Fe}} \approx 1$, $\gamma_{\text{FeS}} \approx 1.5$ (8)

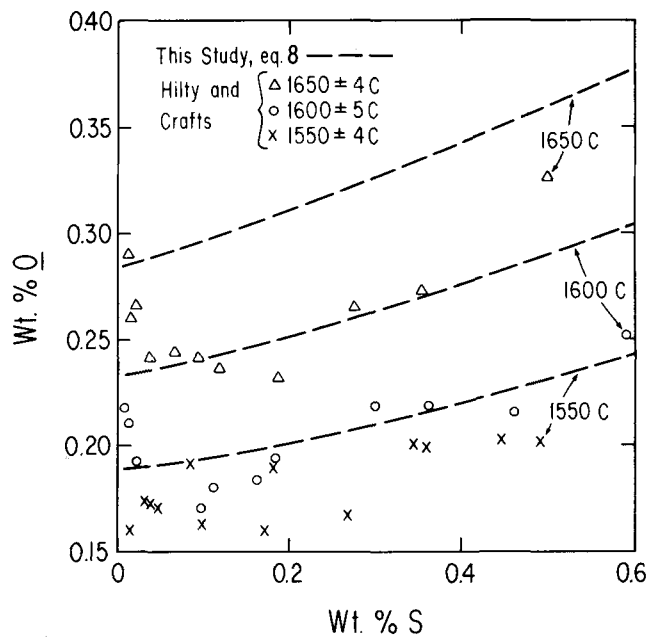


Fig. 5—Effect of sulfur on the solubility of oxygen in liquid iron at saturation with oxysulfide. Points are from Hilty and Crafts.⁹

phase to that in the metal for the compositions in Table IV ranges from 4.5 at 1500 °C to 4.2 at 1650 °C. Experiments in MgO crucibles by Hilty and Crafts⁹ give values of this ratio that range from 1.9 to 9, with those near 3 predominating. Measurements by Sussman¹⁰ in alumina crucibles gave values of 2.7 to 10, with the average of a total of seven values being 4.9. Rocca, Grant, and Chipman¹¹ show a value of 3.6 for the ratio, but no supporting data are given. It is to be noted that virtually all of the values given in References 9 and 10 are at concentrations of sulfur in the metal well in excess of 0.5 wt pct.

The effect of sulfur on the oxygen content of the metal phase for this study and from Hilty and Crafts study⁹ are shown in Figure 5. Contrary to the results reported in this work, Hilty and Crafts found the solubility of oxygen to decrease sharply with small additions of sulfur, and there is a minimum in the oxygen content at 0.1 wt pct sulfur at 1600 °C. Buzhek and Samarin¹² found that sulfur in the metal in the range of 0 to 0.5 wt pct had no effect on the solubility of oxygen in the metal at saturation with the oxysulfide. However, the differences in the results of these studies are not very large.

The possibility of supersaturation of the liquid alloy with respect to the nonmetallic phase was considered. The reproducibility of the measured saturation temperature with repeated cooling of the specimens and the very small amount of the liquid oxide or oxysulfide phase that formed indicated that there was essentially no undercooling for the process of precipitation. In addition, the contact angle between the two phases appears to be very small. Thus, the energy barrier to the nucleation of the new phase can be considered to be very small.

V. SUMMARY

The composition of the liquid metal phase in the Fe-O and Fe-O-S systems at saturation with respect to the liquid oxide (oxysulfide) phase has been determined in the composition range of 0.08 to 0.50 wt pct oxygen and 0 to 0.50 wt pct sulfur. The range of temperatures covered in the work was from 1378 to 1740 °C. The equation for the concentration of oxygen in the liquid metal when saturated with the liquid oxide in the Fe-O system is

$$\log \text{pct O} = -6358/T + 2.76$$

The relationship between temperature and composition of the saturated liquid is

$$T(\text{K, sat}) = -6358/(\log \text{pct O} - 2.76) + \text{pct S} \\ [-554 - 135(\log \text{pct O} - 2.76)]$$

The equation is valid for the composition range of 0 to 0.50 wt pct sulfur and 0.08 to 0.30 wt pct oxygen and the temperature range of 1480 to 1680 °C.

The composition of the oxysulfide phase has been estimated.

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