Free Energy of Hercynite Formation*

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Synopsis

The slag/metal sulphur equilibrium data at 1 550 °C using lime/alumina slags containing MgO and small amounts of FeO have been used to assess the free energy of formation of hercynite. Thus, for the reaction:

the standard free energy change at 1 550 °C has been calculated as -7 644 cal. This value is compared with the experimental data available in the literature.

I. Introduction

Hercynite, $\text{FeO} \cdot \text{Al}_2\text{O}_3$, is an important constituent formed at various stages of iron and steel making processes. For example, it may occur in solid solution with magnetite in certain commercial sinters.^{1,2)} Moreover, it may be formed as an intermediate metastable phase in the final stages of steel making during deoxidation when aluminium content of steel is low or oxygen content of steel is high.^{3,4)} The free energy of formation of hercynite from its constituent oxides has been studied in detail and certain discrepancies exist among data obtained using different techniques. The present paper, therefore, aims at calculation of the free energy of formation of hercynite from slag/metal sulphur partition data by the application of Flood's ionic theory of slags.

II. Experimental Procedure

The experimental study has been described previously.^{5,6)} Essentially, it consisted of equilibrating 50 g of Armco iron in a magnesia crucible with lime/alumina slag and minor amounts of iron oxide at 1 550 °C in argon atmosphere. Sulphur equilibrium was approached from slag side by incorporating calcium sulphide in slag as well as from metal side by introducing elemental sulphur in metal.

III. Results and Discussion

Let ΔG_1 and ΔG_2 be the free energy changes for the following reactions taking place in lime/alumina slag containing FeO and MgO:

substituting

$$G_{\text{FeO} \cdot \text{Al}_2\text{O}_3} = X \text{ and } G_{\text{CaO} \cdot \text{Al}_2\text{O}_3} + G_{\text{FeO}} - G_{\text{CaO}} = a,$$

we get $\Delta G_1 = (X - a)$, similarly, $\Delta G_2 = (X - b)$ where, $b = G_{\text{MgO} \cdot \text{Al}_2\text{O}_3} + G_{\text{FeO}} - G_{\text{MgO}}$. According to Flood *et al.*⁷⁾

$$\begin{aligned} RT \ln a_{\text{FeO}} &= RT \ln (\mathcal{N}_{\text{Fe}^{++}} \mathcal{N}_{\text{O}^{--}}) \\ &+ \Delta G_1 \mathcal{N}_{\text{Ca}^{++}} \mathcal{N}_{\text{Al}_2\text{O}_4^{--}} \\ &+ \Delta G_2 \mathcal{N}_{\text{Mg}^{++}} \mathcal{N}_{\text{Al}_2\text{O}_4^{--}}. \end{aligned}$$

The standard state for iron oxide is the hypothetical stoichiometric compound in the treatment of Flood *et al.* At 1 550 °C, this equation simplifies to

$$8\,340 \log \gamma_{\text{FeO}} = (X - a) \mathcal{N}_{\text{Ca}^{++}} \mathcal{N}_{\text{Al}_2\text{O}_4^{--}} + (X - b) \mathcal{N}_{\text{Mg}^{++}} \mathcal{N}_{\text{Al}_2\text{O}_4^{--}}$$

hence,

$$X = \frac{8\,340 \log \gamma_{\text{FeO}}}{\mathcal{N}_{\text{Al}_2\text{O}_4^{--}} (\mathcal{N}_{\text{Ca}^{++}} + \mathcal{N}_{\text{Mg}^{++}})} + \frac{a \mathcal{N}_{\text{Ca}^{++}} + b \mathcal{N}_{\text{Mg}^{++}}}{\mathcal{N}_{\text{Ca}^{++}} + \mathcal{N}_{\text{Mg}^{++}}}.$$

From available thermodynamic data (see *Appendix*), $a = -585\,314$ and $b = -582\,123$, hence

$$\begin{aligned} X &= \frac{8\,340}{(\mathcal{N}_{\text{Ca}^{++}} + \mathcal{N}_{\text{Mg}^{++}})} \left[\frac{\log \gamma_{\text{FeO}}}{\mathcal{N}_{\text{Al}_2\text{O}_4^{--}}} - 70.1815 \mathcal{N}_{\text{Ca}^{++}} \right. \\ &\quad \left. - 69.7989 \mathcal{N}_{\text{Mg}^{++}} \right]. \end{aligned}$$

The activity coefficient of iron oxide, γ_{FeO} , is calculated with a knowledge of a_{FeO} obtained from the relation,

$$a_{\text{FeO}} = 39.28 \times \frac{C_s}{L_s}$$

where, C_s : the sulphide capacity of the slag

L_s : the sulphur distribution coefficient, $(\%S)/[a_s]$ at 1 550 °C.⁸⁾

It may be mentioned that the activity of iron oxide is relative to the cation-deficient oxide (wüstite) as the standard state. Values of X were calculated for 25 heats. Although certain odd values appear, most of them lie close to the average value of -582 171.

From the data of Elliott and Gleiser¹¹⁾

$$G_{\text{Fe}} = -25\,005 \text{ cal/g} \cdot \text{atom},$$

$$G_{\text{FeO}}^\dagger = -109\,861 \text{ cal/mol},$$

and $G_{\text{Al}_2\text{O}_3} = -463\,341 \text{ cal/mol}$ at 1 550 °C.

Hence $\Delta G_{\text{FeO} \cdot \text{Al}_2\text{O}_3}$ for the reaction,

* Received March 15, 1982. © 1983 ISIJ

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† The standard state for iron oxide is the non-stoichiometric compound ($\text{Fe}_{0.947}\text{O}$).

can be estimated as $-7\,644$ cal.

1. Reliability of Computation of a_{FeO}

The calculation of a_{FeO} involves L_s and C_s . The former is obtained from the present work while C_s is obtained from the work of Kalyanram and Bell⁽¹²⁾ incorporating the temperature effect on C_s from 1 500 to 1 550 °C.

Schurmann *et al.*⁽¹³⁾ have recently carried out slag/metal sulphur partition studies in lime/alumina melts at 1 600 °C using solid electrolyte of thoria to determine the oxygen activity, $[a_o]$, in the system. Their data are presented in Fig. 1 in the form of sulphur capacity, defined as

$$\frac{(\%S)}{[\%S]} \times [a_o],$$

as a function of lime content of the slag. In the present work oxygen analyses of the melts were not made. However, these data can be converted into sulphur capacity form using the relation $[\%O] = 0.185 \times a_{\text{FeO}}$,^(14,15) the approximation $a_{\text{FeO}} = N_{\text{FeO}}$ for slags low in iron oxide⁽⁵⁾ and assuming Henrian behaviour of oxygen in the metal. The standard state for iron oxide referred here is again wüstite. The present data are also plotted in Fig. 1.

The relation between sulphur capacity and sulphide capacity can be deduced as

$$S \cdot C = K_a K_b C_s f_s$$

where, K_a , K_b : the equilibrium constants of the reactions.

Assuming little temperature effect on a_{CaO} (lime activity), f_s (activity coefficient of sulphur in metal) and γ_{CaS} (activity coefficient of calcium sulphide in slag), it can be shown that

$$\begin{aligned} \frac{S \cdot C^{1873}}{S \cdot C^{1823}} &= \frac{K_a^{1873} \cdot K_b^{1873} \cdot C_s^{1873}}{K_a^{1823} \cdot K_b^{1823} \cdot C_s^{1823}} = 1.0312 \times \frac{C_s^{1873}}{C_s^{1823}} \\ &= 1.0312 \times \frac{K^{1873}}{K^{1823}} = 1.0312 \times 1.1848 \\ &= 1.222 \end{aligned}$$

Fig. 1. Sulphur capacity of CaO/Al₂O₃ slags.

where K denotes the equilibrium constant of the reaction $\text{CaO} + \frac{1}{2} \text{S}_2(g) = \text{CaS} + \frac{1}{2} \text{O}_2(g)$, $\Delta G^\circ = 23\,010 - 1.34 T$.⁽⁶⁾ Similarly, the ratio of sulphur capacity at 1 550 °C to that at 1 500 °C can be calculated as 1.236. Since the lime activity slightly increases with temperature the actual ratios would be slightly higher than the above figures.

From Fig. 1, it can be seen that the ratio of sulphur capacity at 1 600 °C to that at 1 550 °C changes from 1.9 to 1.7 for 38 to 46 % lime. It may be mentioned here that the present slags contained 6 to 12 % MgO picked up from the crucible and the experiments of Schurmann *et al.*⁽¹³⁾ were conducted using alumina crucible. Taking into consideration the slight increasing effect of MgO on sulphide capacity (and hence sulphur capacity) of lime/alumina slags⁽¹²⁾ and the increase of solubility of alumina of about 8 % between 1 550 °C and 1 600 °C,⁽¹⁹⁾ the agreement between the two sets of data can be considered to be excellent. Figure 1 also includes the data of Kalyanram and Bell⁽¹²⁾ on slag/gas work using lime/alumina slags containing 1.5 to 10 % MgO at 1 500 °C and this shows reasonable agreement with the data of Schurmann *et al.*⁽¹³⁾ This lends support to the sulphur distribution data used in the calculations.

Very little information exists on sulphide capacity of CaO-MgO-Al₂O₃ slags so as to check the reliability of the data of Kalyanram and Bell.⁽¹²⁾ However, the data of Kalyanram and Bell⁽¹²⁾ on lime/alumina slags without MgO shows good agreement with those of Richardson *et al.*^(20,21) for lime/alumina slags (Fig. 2). Hence the data of Kalyanram and Bell⁽¹²⁾ on lime/alumina slags can be considered reliable. Since Kalyanram and Bell⁽¹²⁾ have used similar experimental technique and procedure for determining the sulphide capacities of CaO-MgO-Al₂O₃ slags, it is logical to

Fig. 2. Effect of mol fraction of lime on sulphide capacity of CaO/Al₂O₃ slags at 1 500 °C.

consider their data on such slags reliable.

2. Comparison with Previous Investigations

Pillay *et al.*²²⁾ measured the steam/hydrogen ratio and oxygen content of liquid iron in equilibrium with alumina and hercynite. Their P_{H_2O}/P_{H_2} at 1 700 °C have been combined with those of Floridis and Chipman²³⁾ at 1 550 and 1 600 °C and that of Thurner²⁴⁾ at 1 586 °C to derive the effect of temperature on the equilibrium constant. The experimental set up remaining the same, the researcher who had done the work at each temperature was different. Hence there is some uncertainty in the earlier work of Pillay *et al.*²²⁾ Pehlke²⁵⁾ assessed the oxygen content in presence of hercynite at 1 606 °C from the appearance of the crucible and combined this data with those of Taylor and Chipman¹⁴⁾ to derive the equilibrium constant at this temperature. The oxygen contents of liquid iron in equilibrium with hercynite were measured by McLean and Ward²⁶⁾ in the temperature range 1 550 to 1 700 °C. It was reported subsequently that impurities in iron samples, such as silicon, titanium and aluminium having a strong affinity for oxygen hinder the attainment of equilibrium with hercynite.²⁷⁾ The measured oxygen contents in equilibrium with hercynite and alumina were probably lower in presence of impurities in iron and hence higher *K* value thus leading to more negative value in free energy of formation than obtained by others. Elliott²⁸⁾ combined this data²⁶⁾ with those of Turpin and Elliott²⁹⁾ to derive the temperature effect on free energy of formation. In the study by Chan *et al.*³⁰⁾ with solid galvanic cells most of the measurements were made only between 750 °C and 1 390 °C. They extrapolated the results to 1 600 °C incorporating the heat of fusion of iron. Recently Kim and McLean²⁷⁾ have reinvestigated this problem by equilibrating very pure iron with hercynite in alumina crucible under argon atmosphere at temperatures between 1 540 °C

and 1 700 °C and have determined the oxygen contents. Hence their work can be considered to be more accurate than others.

The free energies of formation of hercynite at 1 550 °C as determined by various investigators are given in Table 1. The present calculated value of -7 644 cal is in reasonable agreement with that of Kim and McLean.²⁷⁾ The free energy of formation of hercynite needs knowledge of γ_{FeO} which in turn is derived from N_{FeO} . Therefore, any error in the chemical analysis of low concentrations of FeO would be reflected in the calculation of the results. It may be pointed out here that the ceric sulphate titration method was employed to determine FeO in slags. It may be noted that data from several sources (with their own inherent errors) have been made use of for computation of the results. Furthermore, the calculation depends upon the accuracy of *G* values of FeO and Al₂O₃ either of which are two orders of magnitude lower than the free energy of formation of hercynite. However, the values of (*H_T*-*H₂₉₈*) and (*S_T*-*S₂₉₈*) for calcium aluminate and magnesium aluminate as given by Kelley⁸⁾ (see *Appendix*) are in excellent agreement with (*H_T*-*H₂₉₈*) values of 62 000 and 63 250 cal/mol and (*S_T*-*S₂₉₈*) values of 69.75 and 70.875 cal/mol for calcium aluminate and magnesium aluminate respectively at 1 550 °C as given by the later work of Bonnickson.³¹⁾

IV. Conclusions

- (1) By the application of Flood's ionic theory of slags, the free energy of formation of hercynite has been assessed to be -7 644 cal at 1 550 °C. This is in reasonable agreement with the value of -4 519 cal at the same temperature obtained by Kim and McLean.²⁷⁾
- (2) The present calculations confirm the high consistency of available thermodynamic data on slag and metal which are of interest in the iron making process.

Table 1. Comparison of free energy of formation of hercynite at 1 550 °C.

Investigators	-Δ <i>G</i> °	Method
(1) Pillay <i>et al.</i> ²²⁾	3 787	Measurement of steam/hydrogen ratio and oxygen content of liquid iron in equilibrium with alumina and hercynite at 1 700 °C; combination of their data with those of Floridis and Chipman ²³⁾ at 1 550 and 1 600 °C and Thurner ²⁴⁾ at 1 586 °C.
(2) Pehlke ²⁵⁾	4 290 (at 1 606 °C)	Calculation from metal oxygen content in presence of hercynite at 1 606 °C and combination of this data with those of Taylor and Chipman. ¹⁴⁾
(3) McLean & Ward ²⁶⁾	5 256 (ACC±1 200)	Equilibrating liquid iron with alumina and hercynite under helium atmosphere.
(4) Elliott ²⁸⁾	4 886	Calculation by combining the data of McLean and Ward ²⁶⁾ with those of Turpin and Elliott. ²⁹⁾
(5) Chan <i>et al.</i> ³⁰⁾	5 226	EMF method using solid oxide (Lime-Zirconia) galvanic cells between 750 and 1 390 °C; extrapolation of the results to 1 600 °C.
(6) Kim & McLean ²⁷⁾	4 519 (ACC±500)	Equilibrating pure iron with hercynite in alumina crucible under argon atmosphere between 1 540 °C and 1 700 °C.
(7) Present work	7 644	Calculation from slag and metal analysis after slag/metal equilibrium sulphur partition using available thermodynamic data.

Acknowledgements

The author gratefully acknowledges Prof. H. B. Bell, Department of Metallurgy, University of Strathclyde, Glasgow for his able guidance during the course of this work, Dr. G. Mukherjee, Vice Chairman (Technical), Steel Authority of India Ltd, New Delhi for his keen interest and encouragement, and Dr. S. K. Gupta, Managing Director, Mishra Dhatu Nigam Ltd., Hyderabad for his constructive review and suggestions.

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Appendix

In order to calculate a and b , the free energy changes for the following reactions are required:

From Kelley's compilations,⁸⁾ the following data are available at 1 550 °C:

Compound	$(H_T - H_{298})$ (cal/mol)	$(S_T - S_{298})$ (cal/deg·mol)
CaAl ₂ O ₄	62 211	69.85
MgAl ₂ O ₄	63 547	70.95
CaO	19 090	21.85
MgO	17 900	20.24
Al ₂ O ₃	43 940	49.33

$$\text{Hence } \Delta H_3 = (H_T - H_{298})_{\text{CaAl}_2\text{O}_4} - (H_T - H_{298})_{\text{CaO}} - (H_T - H_{298})_{\text{Al}_2\text{O}_3} + (\Delta H_3)_{298}$$

since $(\Delta H_3)_{298} = -3\,600$ cal/mol,⁹⁾ $\Delta H_3 = -4\,419$ cal/mol

similarly, ΔS_3 can be calculated as 4.22 cal/deg·mol taking $(\Delta S_3)_{298} = 5.55$ cal/deg·mol⁹⁾

hence $\Delta G_3 = \Delta H_3 - T \Delta S_3 = -12\,112$ cal.

Since $(\Delta H_4)_{298} = -7\,000$ cal/mol,¹⁰⁾ $\Delta H_4 = -5\,293$ cal/mol at 1 550 °C.

Since $(\Delta S_4)_{298} = 0.61$ cal/deg·mol,⁹⁾ $\Delta S_4 = 1.99$ cal/deg·mol at 1 550 °C.

Hence $\Delta G_4 = -8\,921$ cal/mol.

Using the values of $G_{\text{FeO}} = -109\,861$ cal¹¹⁾ and $G_{\text{Al}_2\text{O}_3} = -463\,341$ cal¹¹⁾

$$a = \Delta G_3 + G_{\text{FeO}} + G_{\text{Al}_2\text{O}_3} = -585\,314$$

$$\text{and } b = \Delta G_4 + G_{\text{FeO}} + G_{\text{Al}_2\text{O}_3} = -582\,123$$