Note

Theoretical Considerations on the Fragmentation of Magnetite Formed during Gaseous Reduction of Hematite

1. Introduction

The products formed during solid state reduction of Fe_2O_3 by iron are Fe_xO and Fe_3O_4 . During gaseous reduction an additional reaction takes place at the $\text{Fe}_x\text{O}/\text{hydrogen}$ boundary. In a recent work¹⁾ it was mathematically proven that a porous (or fragmented) layer of Fe_3O_4 forms on Fe_2O_3 during the initial stages of solid state reduction by iron owing to large-scale migration of iron ions. Such a phenomenon was also experimentally verified in the laboratory investigations involving SEM studies of the partially reduced samples of Fe_2O_3 by iron.²⁾ Schwenk and Rahmel³⁾ proposed a model for oxidation of iron which was based on rate equations for reactions involving unit cells balanced with respect to mass, charge and lattice sites. This approach can be modified and combined with the work in Ref. 1) to make a new model for hydrogen reduction of Fe_2O_3 . The modifications should take into account the following aspects:

(a) The final reaction product in hydrogen reduction is Fe, in contrast to the Fe_xO in solid state reduction and the Fe_2O_3 in oxidation.

(b) Hydrogen, unlike oxygen, cannot be accommodated in the lattices of Fe_2O_3 and Fe_3O_4 for the reasons of thermodynamic stability. In fact oxygen is removed by hydrogen from the $\text{Fe}_x\text{O}/\text{H}_2$ interface.

(c) The reaction at the $\text{Fe}_x\text{O}/\text{H}_2$ interface does not involve the same species as at the $\text{Fe}_2\text{O}_3/\text{O}_2$ interface; in the latter case the migration of oxygen ion vacancies in Fe_2O_3 plays an important role whereas in the former it is the iron ion vacancy.

2. Analysis

Structurally, in addition to the normal lattice sites ($\text{Fe}_{\text{Fe}}^\times$, $\text{O}_{\text{O}}^\times$), the Fe_2O_3 contains³⁾ positively charged oxygen ion vacancies ($\text{V}_{\text{O}}^\bullet$), iron ion interstitials ($\text{Fe}_i^{\bullet\bullet}$), and free electrons (e'). Similarly, Fe_3O_4 contains electron holes (h') and 2 types of iron ion vacancies, V_{Fe}'' and V_{Fe}''' , respectively, with negative charges of 2 and 3. Wustite contains iron ion vacancies, V_{Fe}'' .

Different phases and phase boundaries during gaseous reduction are schematically shown in Fig. 1 wherein the phase boundaries are designated as:

The phase boundary IV, as explained later, will

not exist if it is assumed that hydrogen diffuses through porous iron layer and comes in direct contact with Fe_xO . The phases are identified as follows:

The following simplifying assumptions are made in the model:

- (i) The oxide phases are homogeneous.
- (ii) The Fe/O ratios are constant at the phase boundaries I, II.
- (iii) The iron layer is porous and allows direct contact of hydrogen with wustite, *i.e.*, free passage of gases.
- (iv) The phase transformations and the mass transfers occur across the phase boundaries to maintain local Fe/O ratios.
- (v) Possible gaseous transport *via* physical defects is neglected.

The balanced equations in terms of defects and unit cells are summarized in Table 1. Each reaction contributes to the growth rate of different phases as summarized in Table 2. On the basis of Table 2 the equations for individual phases can be written as:

$$I_A = -4i_1 - 3i_3 - 4i_4 + 8i_5 \quad \dots\dots\dots(1)$$

$$I_B = 3i_1 + 2i_3 + 3i_4 - (6i_5 + i_7) \quad \dots\dots\dots(2)$$

$$I_C = 4i_7 - i_8 \quad \dots\dots\dots(3)$$

$$I_D = i_8 \quad \dots\dots\dots(4)$$

By balancing the defects formed and consumed at different phase boundaries (shown in Table 1) one can write:

$$i_3 = 0 \quad ; \quad \text{by balancing } V_{\text{O}}^{\bullet\bullet} + 2e' \quad \dots\dots\dots(5)$$

$$2i_2 = i_4 \quad ; \quad \text{by balancing } \text{Fe}_i^{\bullet\bullet} + 3e' \quad \dots\dots\dots(6)$$

$$i_5 = i_6 \quad ; \quad \text{by balancing } V_{\text{Fe}}'' + V_{\text{Fe}}''' + 5h' \quad \dots\dots\dots(7)$$

$$i_1 + i_7 = 2i_6 + i_8 \quad ; \quad \text{by balancing } V_{\text{Fe}}'' + 2h' \quad \dots\dots\dots(8)$$

From Eqs. (1) to (8) one gets:

$$I_A = 8i_6 - 4i_1 - 4i_4 \quad \dots\dots\dots(9)$$

$$I_B = 4i_1 + 3i_4 - (8i_6 + i_8) \quad \dots\dots\dots(10)$$

$$I_C = 8i_6 + 3i_8 - 4i_1 \quad \dots\dots\dots(11)$$

$$I_D = i_8 \quad \dots\dots\dots(12)$$

From overall mass balance the net growth rate of iron equivalent (I_{Fe}) and oxygen equivalent (I_{O}) can

Fe_2O_3 (A)	Fe_3O_4 (B)	Fe_xO (C)	Fe (D)	H_2
I	II	III	IV	

Fig. 1. Different phases and phase boundaries.

Table 1. Phase boundary reactions in hydrogen reduction of Fe_2O_3 .

Bound-ary	Rate	Reaction equation	Reaction
I	i_1	$4\text{Fe}_2\text{O}_3 + [\text{Fe}_{\text{Fe}}^{\text{Fe}}]_B = 3\text{Fe}_3\text{O}_4 + [V_{\text{Fe}}'' + 2h']_B$	(1)
I	i_2	$\text{Fe}_2\text{O}_3 + 2(V_i)_A = [2\text{Fe}_i^{\text{Fe}} + 6e' + 3\text{O}_2]_A$	(2)
I	i_3	$2\text{Fe}_2\text{O}_3 + [2\text{Fe}_{\text{Fe}}^{\text{Fe}} + V_{\text{O}}'' + 2e' + 2\text{O}_2]_A = 2\text{Fe}_3\text{O}_4$	(3)
I	i_4	$4\text{Fe}_2\text{O}_3 + [\text{Fe}_i^{\text{Fe}} + 3e']_A = 3\text{Fe}_3\text{O}_4 + (V_i)_A$	(4)
I	i_5	$5\text{Fe}_3\text{O}_4 + [V_{\text{Fe}}'' + V_{\text{Fe}}''' + 5h' + \text{Fe}_{\text{Fe}}^{\text{Fe}} + 4\text{O}_2]_B = 8\text{Fe}_2\text{O}_3$	(5)
II	i_6	$\text{Fe}_3\text{O}_4 + [2V_{\text{Fe}}'' + 4h']_C = 2\text{FeO} + [V_{\text{Fe}}'' + V_{\text{Fe}}''' + 5h' + \text{Fe}_{\text{Fe}}^{\text{Fe}} + 4\text{O}_2]_B$	(6)
II	i_7	$\text{Fe}_3\text{O}_4 + [\text{Fe}_{\text{Fe}}^{\text{Fe}}]_C = 4\text{FeO} + [V_{\text{Fe}}'' + 2h']_C$	(7)
III	i_8	$\text{FeO} + [V_{\text{Fe}}'' + 2h']_C + \text{H}_2 = \text{Fe} + \text{H}_2\text{O}$	(8)

V_i : The unoccupied interstitial position

Table 2. Balance equations for the growth of different phases.

Bound-ary	Reaction	Fe_2O_3	Fe_3O_4	FeO	Fe
I	(1)	$-4i_1$	$+3i_1$		
I	(2)	$-i_2 + i_2$			
I	(3)	$-3i_3$	$+2i_3$		
I	(4)	$-4i_4$	$+3i_4$		
I	(5)	$+8i_5$	$-6i_5$		
II	(6)		$+i_6 - i_6$	$-2i_6 + 2i_6$	
II	(7)		$-i_7$	$+4i_7$	
III	(8)			$-i_8$	$+i_8$

be written as:

$$I_{\text{Fe}} = 3I_B + I_C + 2I_A$$

On substituting the respective values,

$$I_{\text{Fe}} = i_4 \quad \text{.....(13)}$$

Similarly,

$$I_0 = 3I_A + 4I_B + I_C = -i_8 \quad \text{.....(14)}$$

Eqs. (13) and (14) demonstrate that the equations in Table 1 are balanced. Further, I_{Fe} and I_0 signify net rates of iron and oxygen transfer, respectively, through the phase boundaries in the opposite directions. Under the conditions of constant rate of reduction:

$$i_4 = -i_8 \quad \text{.....(15)}$$

Substituting this in Eqs. (9) to (11) one obtains,

$$I_A = 8i_6 - 4i_1 + 4i_8 \quad \text{.....(16)}$$

$$I_B = 4i_1 - 4i_6 - 8i_8 \quad \text{.....(17)}$$

$$I_C = 8i_6 + 3i_8 - 4i_1 \quad \text{.....(18)}$$

If it is assumed that the layers of different oxides reduce orthogonally (similar to that in oxidation of iron), then the layer thickness, number of unit cells and their changes become proportional. The layer thickness can be expressed in terms of number of unit cells per unit area multiplied by the molar volume of

the phase involved. Based on this³⁾ one can write the following relationship:

$$I_B/I_C = (S_{\text{Fe}_3\text{O}_4}/S_{\text{Fe}_3\text{O}}) \times (V_{\text{Fe}_3\text{O}}/V_{\text{Fe}_3\text{O}_4}) \quad \text{.....(19)}$$

where, S_{oxide} : layer thickness of oxide phase

V_{oxide} : molar volume of oxide.

The approximate values of molar volumes are

$$V_{\text{Fe}_3\text{O}_4} = 44.7 \text{ cm}^3 \text{ mol}^{-1}$$

$$V_{\text{Fe}_3\text{O}} = 12.2 \text{ cm}^3 \text{ mol}^{-1}$$

The values of $S_{\text{Fe}_3\text{O}_4}$ and $S_{\text{Fe}_3\text{O}}$ can be obtained from experimental data. Let,

$$I_B/I_C = t \quad \text{.....(20)}$$

Any 3 of the 4 equations, (16)–(18) and (20), can now be used to eliminate I_A , I_B , and I_C to yield,

$$i_1 = i_8 [0.75 + \{0.25/(t+1)\}] + 2i_6 \quad \text{.....(21)}$$

The values of i_6 and i_8 can be obtained by using Wagner's model for a diffusion controlled process.¹⁾

3. Discussion

The oxidation and reduction processes differ with regard to reactions at $\text{Fe}_2\text{O}_3/\text{O}_2$ and $\text{Fe}_x\text{O}/\text{Fe}$ phase boundaries. According to Eq. (5), $i_3=0$, i.e., the oxygen vacancies in Fe_2O_3 have no role to play in reduction (see reaction (3) in Table 1). Instead, the reduction reactions proceed by iron ion migration (via reactions (1) and (5) to (7) in Table 1).

Eq. (21) describes the dependence of the phase boundary reaction (1) on reactions (6) and (8) only (see Table 1). The implications of Eq. (21) are as follows:

(1) The contributions of reactions (2)–(5) and (7) in Table 1 cancel out in the reduction process.

(2) Reaction (6) shows that the transformation of Fe_3O_4 to Fe_xO takes place by migration of iron ion vacancies within Fe_3O_4 .

(3) Reaction (8) shows that the reduction of Fe_xO to Fe takes place by migration of iron vacancies within Fe_xO .

(4) Reaction (1) shows that the transformation of Fe_2O_3 to Fe_3O_4 proceeds by solid state diffusion of iron ions in Fe_3O_4 .

Bitsaines and Joseph⁴⁾ carried out experiments on reduction of Fe_2O_3 by hydrogen at 1 023 K and observed that the layers of iron oxides formed topographically. On macro scale the layers of various oxides appeared to be sharply defined and from their experiment,

$$S_{\text{Fe}_3\text{O}} = 0.055 \text{ cm}; \quad S_{\text{Fe}_3\text{O}_4} = 0.008 \text{ cm}$$

From Eqs. (19) and (20),

$$t = (0.008/0.055) \times (12.2/44.7) = 0.0397$$

Substituting the above values of t in Eq. (21)

$$i_1 = 0.99i_8 + 2i_6 \quad \text{.....(22)}$$

The values of i_6 and i_8 at 1 023 K can be obtained from Refs. 1), 5), and 6) as,

$$i_6 = 1.0489 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1} \quad \text{.....(23)}$$

$$i_8 = 2.732 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1} \quad \text{.....(24)}$$

Eqs. (23) and (24) show that at 1 023 K i_8 is greater than i_6 almost by a factor of 26 which on inserting in Eq. (22) would lead to the conclusion that in hydrogen reduction of hematite at 1 023 K the rate controlling step is either reaction (8) (see Table 1) at the $\text{Fe}_x\text{O}/\text{Fe}$ interface or reaction (1) at the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ interface. Reaction (1) proceeds, as also indicated in earlier work,¹⁾ by solid state diffusion of iron ions in Fe_3O_4 towards Fe_2O_3 and results in the fragmentation of Fe_3O_4 , thereby increasing the surface area and hence the surface diffusion of iron in Fe_3O_4 . Under these conditions the reduction at $\text{Fe}_x\text{O}/\text{Fe}$ interface could be rate controlling rather than at $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ interface.

In the above calculations it has been *a priori* assumed that the iron layer is porous. If this is not the case, then the reduction process can become controlled jointly by mass transfer of gas in the iron formed on wustite and by chemical reaction at the $\text{Fe}_x\text{O}/\text{Fe}$ interface. Under the conditions of extremely low porosity it would be predominantly gas diffusion controlled. A change in the rate controlling step will thus occur merely on account of extent of porosity of iron layer formed on wustite. The genesis of porosity formation has been discussed in detail elsewhere.⁷⁾

It is clear from the above discussion that irrespective of the rate controlling steps the basic mechanism of the reaction at $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ interface does not change. When gaseous reduction takes place the fragmentation of Fe_3O_4 will occur.

4. Conclusions

The model based on phase boundary reactions and

mass transfer clearly describes the contribution of various reactions during gaseous reduction of Fe_2O_3 . The transformations of Fe_xO to Fe and of Fe_3O_4 to Fe_xO essentially take place by migration of iron ion vacancies whereas the transformation of Fe_2O_3 to Fe_3O_4 occurs by solid state diffusion of iron ions. During gaseous reduction of Fe_2O_3 the cracking of Fe_3O_4 is theoretically predicted.

REFERENCES

- 1) B. Deo, R. K. Dube and S. Chatterjee: *ISIJ Int.*, **29** (1989), 345.
- 2) S. Chatterjee: Master Tech. Thesis, Indian Inst. of Technol., Kanpur, (1988).
- 3) W. Schwenk and A. Rahmel: *Oxidation of Metals*, **25** (1986), 293.
- 4) G. Bitsaines and T. L. Joseph: *J. Met.*, **7** (1955), 639.
- 5) C. Wagner: *Prog. Solid State Chem.*, **10** (1975), 3.
- 6) C. Wagner: *Acta metall.*, **17** (1969), 99.
- 7) R. K. Dube and Brahma Deo: *Steel Res.*, **58** (1987), 395.

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