

# Reduction of Solid Wustite in H<sub>2</sub>/H<sub>2</sub>O/CO/CO<sub>2</sub> Gas Mixtures

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The reduction of dense wustite in H<sub>2</sub>/H<sub>2</sub>O/CO/CO<sub>2</sub> gas mixtures has been carried out at temperatures between 1073 and 1373 K. The critical conditions for the formation of porous iron product morphologies have been identified and the results discussed in relation to the breakdown of dense iron layers on wustite surfaces.

## I. INTRODUCTION

IN previous studies<sup>[1-4]</sup> of wustite reduction in H<sub>2</sub>/H<sub>2</sub>O and CO/CO<sub>2</sub> gas mixtures, three main product microstructures were identified. These structures are porous iron (type A), porous wustite covered with dense iron (type B), and dense wustite covered with dense iron (type C). Type B structures have been shown to result from the decomposition of the dense wustite prior to iron nucleation. The decomposition reaction results in the formation of relatively coarse tunnels throughout the material, and the surfaces of these tunnels are subsequently covered with a dense iron layer.

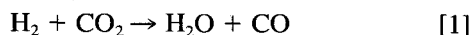
In industrial reduction processes, all of the gas species H<sub>2</sub>/H<sub>2</sub>O/CO/CO<sub>2</sub> are present in the systems, in various proportions. For example, hydrogen and steam are to be found in iron blast furnace gases due to the humidity of the air blast and the addition of hydrocarbon injectants.<sup>[5]</sup> Direct reduction processes utilize hydrocarbon sources as reductants again producing complex H<sub>2</sub>/H<sub>2</sub>O/CO/CO<sub>2</sub> gas mixtures.<sup>[6]</sup>

The aim of the present study then is to determine the gas and temperature conditions necessary to produce porous iron product morphologies in these complex gas mixtures.

## II. EXPERIMENTAL

A detailed description of the apparatus and experimental procedure used in the present investigation has been previously published.<sup>[7]</sup> Pure dense 1-mm<sup>3</sup> wustite samples ( $y = 0.10$ ) were reduced in a novel design reaction furnace which enables fast quenching of the samples after a given reaction time.

The H<sub>2</sub>/H<sub>2</sub>O and CO/CO<sub>2</sub> ratios in each reduction gas mixture were chosen so as to produce a chosen oxygen partial pressure in the gas mixture from both sets of components at the reaction temperature under investigation;<sup>[8]</sup> *i.e.*, the reaction



is at equilibrium. These individual H<sub>2</sub>/H<sub>2</sub>O and CO/CO<sub>2</sub>

gas flows are then combined prior to introduction into the reaction chamber. The flows in the gas streams were chosen such that the volumetric ratios (H<sub>2</sub> + H<sub>2</sub>O)/(CO + CO<sub>2</sub>) = 1/9, 1/1, 4/1, 9/1, and 19/1 were produced in the final gas mixtures, having a total flow rate of 1 L min<sup>-1</sup>.

Following reduction, the partially reduced samples were mounted in ARALDITE\* containing approximately

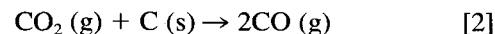
\*ARALDITE is a trademark of Ciba-Geigy Corporation, Hawthorne, NY.

20 wt pct alumina powder ( $-50 \mu\text{m}$ ), polished using 1- $\mu\text{m}$  diamond paste, and examined by conventional optical microscopy.

## III. RESULTS AND DISCUSSION

### A. Porous/Dense Iron Transition

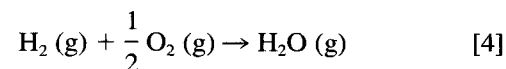
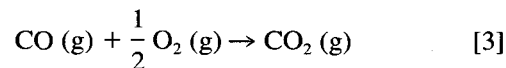
The critical gas compositions for porous iron formation on reduction of wustite in H<sub>2</sub>/H<sub>2</sub>O/CO/CO<sub>2</sub> gas mixtures at temperatures between 1073 and 1373 K have been determined by the examination of partially reduced oxide samples. These critical conditions are presented in Table I and also as a function of carbon activity (Figure 1) and oxygen potential (Figure 2) in the gas mixtures at the various reaction temperatures. The activities of carbon, given relative to solid graphite, are calculated<sup>[8]</sup> assuming equilibrium for the reaction



*i.e.*,

$$a_c = \frac{1}{K_2} \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}}$$

The oxygen potentials of the gas mixtures are determined through the equilibria



*i.e.*,

$$P_{\text{O}_2}^{1/2} = \frac{1}{K_3} \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = \frac{1}{K_4} \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$$

for any given reaction temperature.

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Manuscript submitted December 23, 1988.

**Table I. Summary of the Critical Conditions for the Formation of a Porous Iron Product on Reduction of Wustite in H<sub>2</sub>/H<sub>2</sub>O/CO/CO<sub>2</sub> Gas Mixtures (Total Pressure 100 kPa)**

Temperature (K)	Gas Composition (Vol Pct)			
	H <sub>2</sub>	H <sub>2</sub> O	CO	CO <sub>2</sub>
			$\frac{H_2 + H_2O}{CO + CO_2} = 0$	
1073	—	—	92.2	7.8
1173	—	—	91.8	8.1
1273	—	—	90.6	9.4
1373	—	—	83.3	16.7
			$\frac{H_2 + H_2O}{CO + CO_2} = \frac{1}{9}$	
			carbon deposition	
1073	—	—	—	—
1173	9.2	0.8	81.0	9.0
1273	8.2	1.8	62.6	27.4
1373	7.8	2.2	44.5	35.5
			$\frac{H_2 + H_2O}{CO + CO_2} = 1$	
1073	46.3	3.7	45.9	4.1
1173	42.9	7.1	44.0	6.0
1273	36.0	14.0	40.4	9.6
1373	30.1	19.9	39.2	10.8
			$\frac{H_2 + H_2O}{CO + CO_2} = \frac{4}{1}$	
1073	73.7	6.2	18.0	2.0
1173	66.4	13.6	17.1	2.9
1273	54.2	25.8	16.0	4.0
1373	48.2	31.8	15.5	4.5
			$\frac{H_2 + H_2O}{CO + CO_2} = \frac{9}{1}$	
1073	83.3	6.7	9.2	0.8
1173	77.2	12.8	8.8	1.2
1273	62.2	27.8	7.9	2.1
1373	54.2	35.8	7.7	2.3
			$\frac{H_2 + H_2O}{CO + CO_2} = \frac{19}{1}$	
1073	91.3	3.7	4.8	0.2
1173	82.3	12.7	4.4	0.6
1273	65.7	29.3	3.9	1.1
1373	62.0	33.0	3.8	1.2
			$\frac{H_2 + H_2O}{CO + CO_2} = \infty$	
1073	>99.5	<0.5	—	—
1173	>99.5	<0.5	—	—
1273	71.1	28.9	—	—
1373	60.3	39.7	—	—

It should be noted that while the oxygen potential of the system varies with the ratio of the partial pressures of the gases and is independent of the total (CO + CO<sub>2</sub>) pressure, the activity of carbon at any CO/CO<sub>2</sub> ratio depends on the partial pressures of the species.

Provided equilibrium is attained between the iron and the gas mixtures, the carburization of iron should result in  $\gamma$ -iron being the stable form over most of the reaction conditions studied using those complex H<sub>2</sub>/H<sub>2</sub>O/CO/CO<sub>2</sub> mixtures. The conditions for the  $\alpha$ - to  $\gamma$ -iron transition marked on Figure 1 are derived from data by Smith.<sup>[9]</sup>

It can be seen (Figure 1) that the critical carbon activities required to produce porous iron decrease progressively with increasing (H<sub>2</sub> + H<sub>2</sub>O) in the gas mixtures, and that at any (H<sub>2</sub> + H<sub>2</sub>O)/(CO + CO<sub>2</sub>) ratio the critical carbon activity decreases with increasing temperature. At 1073 K, it appears that the critical carbon activity at high (H<sub>2</sub> + H<sub>2</sub>O)/(CO + CO<sub>2</sub>) ratios remains constant at a value sufficient to maintain the existence of  $\gamma$ -iron. However, this latter observation should be treated with caution, because small variations in CO<sub>2</sub> flow rate (e.g., 1 to 2 ml min<sup>-1</sup>) at high (H<sub>2</sub> + H<sub>2</sub>O)/(CO + CO<sub>2</sub>)

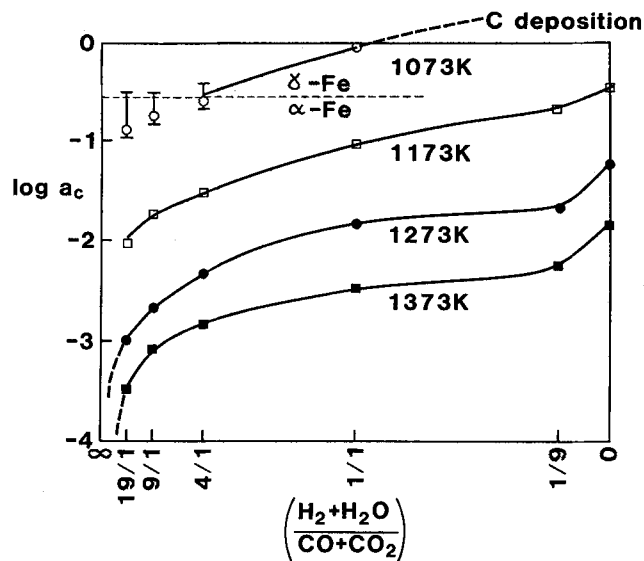


Fig. 1—Conditions for the formation of porous iron in ( $H_2 + H_2O + CO + CO_2$ ) mixtures as a function of the carbon activity of the gas (total pressure 100 kPa).

ratios can lead to significant changes to the carbon activity of the gas. This uncertainty is reflected in the error bars for these conditions in Figures 1 and 2.

In contrast to the lack of any clear correlation between carbon activity and the porous/dense iron transition at any particular temperature, the transition appears to occur

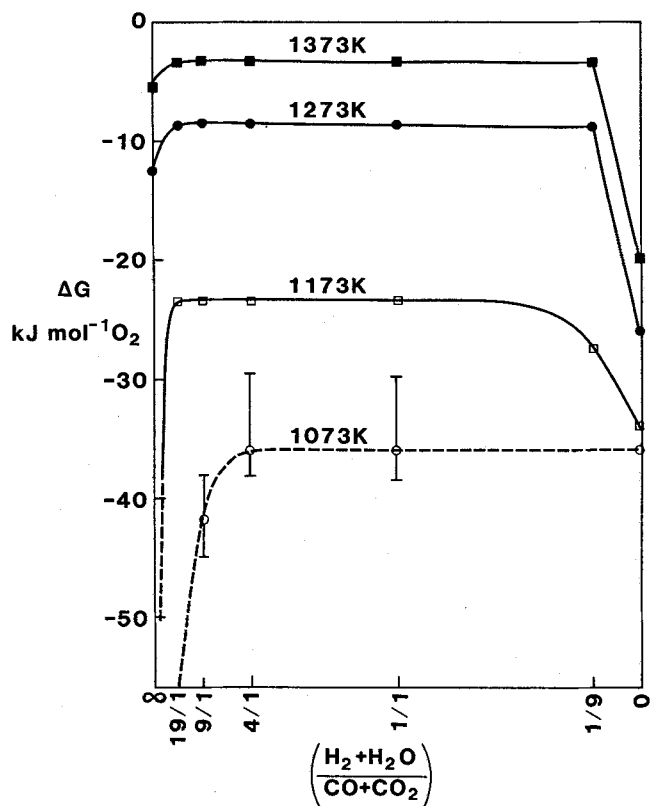


Fig. 2—Conditions for the formation of porous iron in ( $H_2 + H_2O + CO + CO_2$ ) mixtures as a function of the oxygen potential of the gas (total pressure 100 kPa).

at a critical oxygen partial pressure over a wide range of ( $H_2 + H_2O$ )/( $CO + CO_2$ ) gas ratios (Figure 2). The results indicate that the presence of even low concentrations of ( $H_2 + H_2O$ ) in  $CO/CO_2$  mixtures decreases the oxygen potential required for the production of porous iron, especially above 1173 K. The presence of ( $CO + CO_2$ ) in the  $H_2/H_2O$  gas mixtures significantly reduces the critical oxygen potentials for porous iron growth at temperatures below 1173 K.

### B. Mechanisms of Breakdown of Dense Iron Layers

In an earlier study,<sup>[3]</sup> it was concluded that the critical step in the breakdown of iron layers in the  $H_2/H_2O$  system was void nucleation at the iron/wustite interface, and that this could occur even under conditions where the equilibrium gas pressures at the  $Fe/FeO$  interface were less than the total pressure of the reducing gas. In  $CO/CO_2$  gas mixtures, the carbon activity was shown to have a major influence on iron layer breakdown, and the critical carbon activity was found to increase significantly with decreasing chemical reaction rate, *i.e.*, decreasing  $CO$  partial pressures.

With the formation of a dense iron layer, there is no longer any direct contact between the reaction gas and the wustite. The oxygen concentration in the iron at the  $Fe/FeO$  interface is that in equilibrium with wustite. The oxygen concentration in the iron at the gas/ $Fe$  interface is dependent on the relative rate of oxygen removal by chemical reaction with the gas at the iron surface and the flux of oxygen through the dense iron layer to the gas/ $Fe$  interface.

The transfer of an oxygen atom from the  $Fe/FeO$  interface to the gas/metal interface results in the creation of a vacant oxygen lattice site in the wustite at the iron/wustite interface (Figure 3). If a number of these vacancies combine to form a vacancy cluster or void, this may act as a possible site for the nucleation of a gas bubble at the interface. The probability of forming a vacancy cluster of any given size will increase with the population of vacancies at the interface. The vacancy population, in turn, is dependent on the relative rates of formation and elimination of vacant sites. Vacant sites at the interface are eliminated through the occupation of the sites by neutral iron atoms, which, in turn, results in the advancement of the  $Fe/FeO$  interface.

If the chemical reaction rate on the iron surface is fast

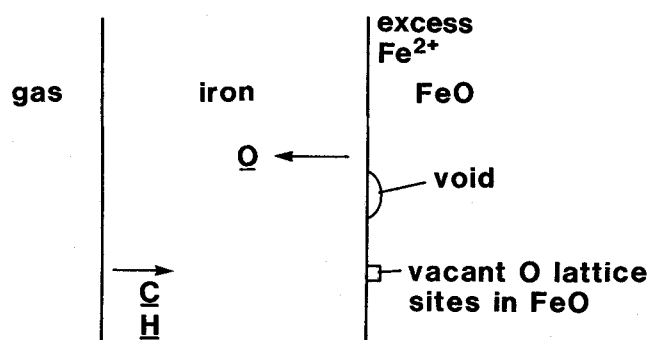


Fig. 3—Condensed species present during the growth of an iron layer on wustite.

compared to the oxygen mass transport through the iron, then the oxygen concentration at the surface approaches that in equilibrium with the gas mixture (Figure 4(a)), and the reaction rate is mass-transport limited. If the chemical reaction rate is slow compared to the oxygen mass transport through the solid iron, the oxygen concentration in the iron will tend toward that in equilibrium with wustite (Figure 4(c)), and the reaction rate is chemical-reaction-rate limited.

From Fick's first law, the diffusive flux of oxygen to the metal surface through the dense iron layer,  $J_O$ , is given by the expression

$$J_O = D_O^{Fe} \frac{(C_O^{FeO} - C_O^{Surf})}{x} \text{ moles m}^{-2} \text{ s}^{-1} \quad [5]$$

where  $C_O^{FeO}$  = the oxygen concentration in iron in equilibrium with FeO (moles  $\text{m}^{-3}$ );

$C_O^{Surf}$  = the oxygen concentration in iron at the gas/metal interface (moles  $\text{m}^{-3}$ );

$D_O^{Fe}$  = the diffusion coefficient of oxygen in solid iron ( $\text{m}^2 \text{s}^{-1}$ ); and

$x$  = the thickness of the dense iron layer (m).

For any reaction temperature, the dependent variables in this expression are the concentration of oxygen at the gas/metal interface,  $C_O^B$ , and the thickness of the iron layer. The oxygen flux increases as  $C_O^B \rightarrow 0$  and  $x \rightarrow 0$ . The maximum possible rate of removal of oxygen from any surface, however, is determined by the chemical reaction rate at the gas/metal interface. Thus, the overall rate of removal of oxygen from a surface varies as a function of iron layer thickness, as illustrated schematically in Figure 5.

A high vacancy population at the Fe/FeO interface, and it follows a high probability of void formation, is favored by high rates of oxygen removal through the iron layer. Thus, it is to be expected that iron layer breakdown occurs readily under conditions of high chemical reaction rates and low oxygen potentials in the reducing gas.

Several other points require further elaboration if the void nucleation model is to explain the experimental observations satisfactorily. According to the description of the rate processes outlined above (Figure 5) for small iron layer thicknesses, the maximum oxygen flux through

the metal will be determined by the chemical reaction rate on the iron surface. From this argument, it is expected that breakdown of the iron layer will be dependent on the hydrogen or carbon monoxide partial pressures in the reducing gas. However, the experimental evidence shows the oxygen potential of this gas to be the critical factor determining iron layer breakdown rather than hydrogen pressure. This apparent contradiction is explained with reference to an earlier paper,<sup>[10]</sup> in which it was shown that dense iron layers of substantial thickness (e.g., 0.1  $\mu\text{m}$ ) are formed during the initial growth of the metal over oxide surfaces. Since the iron forms on wustite, which is supersaturated with iron ions, it is expected that the precipitation of the excess iron ions will make a major contribution to the rapid growth in thickness of the iron layer as it spreads over the oxide surface. Once an iron layer of this magnitude is established, the rate of oxygen removal from the iron/iron oxide interface will be determined by the diffusive flux of oxygen through the iron (i.e., Eq. [5]). The oxygen concentration in iron at the Fe/FeO interface,  $C_O^{FeO}$ , is fixed by the iron/wustite equilibrium, and  $D_O^{FeO}$  is dependent on the reaction temperature and the crystal structure of the iron. Therefore, at any given iron layer thickness, the diffusive flux of oxygen is determined by the oxygen concentration in iron at the gas/iron interface. Under conditions where the chemical reaction rate is high, the oxygen concentration in iron at the surface is that in equilibrium with the oxygen potential of the gas mixture. Thus, it follows that the critical conditions for porous growth of iron in gas mixtures containing  $\text{H}_2/\text{H}_2\text{O}$  are largely determined by the oxygen partial pressure of the gas, which represents the driving force for mass transport through the iron layer.

The chemical reaction rates on iron surfaces in  $\text{CO}/\text{CO}_2$  gas mixtures are very much slower than  $\text{H}_2/\text{H}_2\text{O}$ ,<sup>[11]</sup> and it follows that the rates of oxygen removal are slow compared with void elimination processes. In the case of  $\text{CO}/\text{CO}_2$  mixtures, it might be expected from the above arguments that breakdown of the iron layers will only occur at very low oxygen partial pressures. The experimental evidence, however, shows breakdown to occur at quite high oxygen partial pressures. A moment's consideration shows these results can still be reconciled with the void nucleation model. Through Eq. [1], it can be

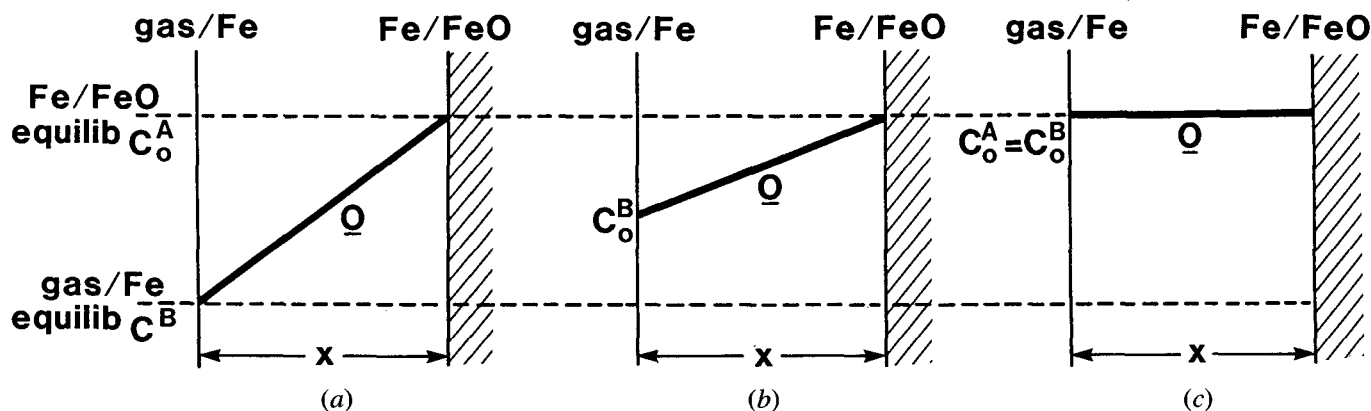


Fig. 4—Schematic representation of the oxygen profiles across a dense iron layer formed on wustite where the oxygen removal is limited by (a) mass transport in the iron, (b) mixed chemical reaction/mass transport, and (c) chemical reaction with the gas.

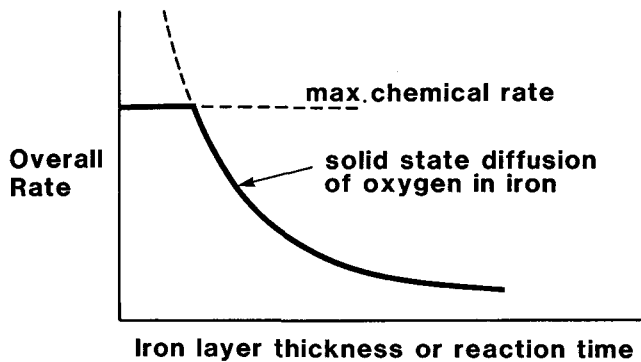


Fig. 5—The effect of iron layer thickness and reaction time on the overall rate of removal of oxygen from an iron surface formed on wustite.

seen that the carbon activities in the iron layer are determined by the  $\text{CO}/\text{CO}_2$  gas mixtures. It has been shown<sup>[3,12]</sup> that the equilibrium gas pressures at the iron/wustite interface in these systems can be quite high. It is argued that as a result of these high pressures, the critical void size for bubble nucleation at the iron/wustite interface in  $\text{CO}/\text{CO}_2$  gas mixtures is smaller than in  $\text{H}_2/\text{H}_2\text{O}$  mixtures. Thus, the probability of forming a critically sized void at any given oxygen potential is increased. This would account for the breakdown of iron layers at higher oxygen potentials than might otherwise be expected.

In mixed  $\text{H}_2/\text{H}_2\text{O}/\text{CO}/\text{CO}_2$  gas mixtures, because of the high rates of the chemical reactions at the iron surface due to reaction with hydrogen, the critical conditions for breakdown are dominated by the oxygen potential of the gas. At low temperatures, the presence of  $\text{CO}/\text{CO}_2$  gas mixtures can make a significant contribution to the determination of the critical gas conditions for porous growth through (a) the reduction of the critical void size required for breakdown and (b) the stabilization of  $\gamma$ -iron to lower temperatures. The effects of the  $\alpha$ - to  $\gamma$ -iron transition have not yet been unambiguously determined. The formation of  $\gamma$ -iron rather than  $\alpha$ -iron at temperature may be important here; because of the large disregistry, the  $\gamma$ -Fe/FeO interface should make it easier for void nucleation to occur.<sup>[3]</sup> On the other hand, this effect may be offset by the decrease in oxygen permeability on transforming from  $\alpha$ - to  $\gamma$ -iron.<sup>[12]</sup>

#### IV. SUMMARY

The conditions for the formation of porous iron structures have been identified for gas conditions ranging from binary  $\text{H}_2/\text{H}_2\text{O}$ , through complex  $\text{H}_2/\text{H}_2\text{O}/\text{CO}/\text{CO}_2$ , to binary  $\text{CO}/\text{CO}_2$  mixtures at temperatures between 1073 and 1373 K. It has been clearly shown that porous iron morphologies are more readily obtained in  $\text{H}_2/\text{H}_2\text{O}/\text{CO}/\text{CO}_2$  than in binary gas mixtures. The breakdown of dense iron layers on wustite at any given reaction temperature in these complex gas mixtures appears to occur at a critical oxygen potential. The mechanism of breakdown of the dense iron layers is explained in terms of a reaction model involving the nucleation of voids at the iron/wustite interface.

#### ACKNOWLEDGMENTS

The authors wish to thank Hamersley Iron Proprietary Ltd., Perth, Australia and Broken Hill Proprietary Ltd., Melbourne, Australia for their support for this project through the Australian Mineral Industries Research Association.

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