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Limited role of cation bulk diffusion in the oxidation of pure iron to magnetite

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Recent experimental results for the oxidation of pure iron to magnetite below the eutectoid temperature for the formation of wüstite (570 °C) are re-analysed with respect to the mechanisms which control the overall reaction kinetics. The experimental parabolic rate constants are compared with those expected for cation bulk diffusion controlled reaction kinetics. The comparison shows that the experimental rate constants are as much as two orders of magnitude larger than the calculated values suggesting that processes other than cation bulk diffusion contribute to the overall reaction kinetics in the set of experiments investigated.

1. Introduction

In the oxidation of a pure metal, there are several possible processes which may affect the overall reaction kinetics. For example, the transport of cations or anions through the product layer may yield a parabolic rate law. If the layer is thin and diffusion is very quick, a linear rate law may result. Other processes which may affect the overall reaction kinetics, for example, are the adsorption and the desorption of gas molecules at the oxide surface and their transport in the gas phase; the former two may be particularly sensitive to the surface characteristics of the oxide being formed [1].

In the case of diffusion-controlled reaction kinetics, the parabolic rate law

$$\Delta x^2 = 2k_p t \qquad (1)$$

is applicable in describing the increase in product layer thickness, Δx, as a function of time t, independent of the type of the rate-limiting diffusional transport; k_p is the parabolic rate constant. Gemma *et al.* [2] have recently published new experimental results which show that the oxidation of pure iron to magnetite at temperatures near the eutectoid temperature for the formation of wüstite approximates parabolic reaction kinetics. However, the mechanism by which the migration occurs is not adequately addressed. Which species are more mobile and to what extent do they move through the bulk of the product layer by point defects or along grain boundaries and other structural defects such as dislocations, pores, etc.? In this paper, the extent to which cation diffusion via point defects in the product layer is important for the oxidation kinetics of metallic iron to magnetite is addressed.

Based on the assumption that the oxidation reaction kinetics are controlled by the diffusion of cations through a bulk product layer, a framework of equations has been developed which allows the calculation of parabolic rate constants for the formation of magnetite ($Fe_{3-\delta}O_4$) [3]. For such a calculation, information about iron tracer diffusion coefficients in magnetite, correlation factors to appropriately account for non-randomness in diffusion processes, oxygen activities corresponding to equilibrium phases in the iron–oxygen system, and the point defect structure of magnetite are needed; a detailed discussion and experimental data for high temperatures are reported [3]. While the data which form the basis for calculations of the parabolic rate constant, k_p, were measured at high temperatures, extrapolations of these data to lower temperatures have been shown to be valid in some cases. Atkinson has shown that an extrapolation of the tracer diffusion data, originally reported in Reference 4, to temperatures as low as 500 °C can still be accomplished while achieving a favourable comparison with experimental tracer diffusion data measured at this temperature [5]. More recently, the framework of equations developed in Reference 3 has been used to compare calculated results to experimentally determined rate constants for the formation of magnetite by the corrosion of iron in aqueous borate solutions for temperatures ranging between 150 °C and 300 °C [6]. While the experimentally determined rate constants are greater than the calculated values, the authors' comparison of the calculated values with experimental rate constants, determined by other investigators, for temperatures around 400 °C shows a relatively good agreement. However, the fact that the predicted activation enthalpy for the formation of magnetite is higher than that experimentally observed suggests that a contribution to transport along grain boundaries, for example, may be very important too.

The purpose of this paper is to compare the new experimental data reported by Gemma *et al.* [2] with the parabolic rate constants calculated by using the data summarized in Reference 3 corresponding to the formation of magnetite below the eutectoid temper-

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ature for the formation of wüstite ($T_{\text{wüs}} = 570\,°\text{C}$). Conclusions concerning the extent to which cation diffusion plays a role in the oxidation kinetics of pure iron will then be made.

2. Defects and diffusion in magnetite

As a transition metal oxide, magnetite exhibits a degree of non-stoichiometry which varies over a range of oxygen activity ($a_{O_2} = P_{O_2}/P°$; $P° \equiv 1$ atm $= 1.013 \times 10^5$ Pa) corresponding to the thermodynamic stability of the phase. Due to a component activity-dependent disorder coupled with a Frenkel equilibrium, different types of point defects predominate as a function of oxygen activity. It has been found that at high oxygen activities cation vacancies predominate ($\delta \propto a_{O_2}^{2/3}$) while cation interstitials predominate ($|\delta| \propto a_{O_2}^{-2/3}$) at low oxygen activities [7, 8]. The deviation from stoichiometry, δ, in magnetite, $Fe_{3-\delta}O_4$, is the difference in concentrations of these predominant point defects. When plotted against the logarithm of oxygen activity, δ has the form of an "S-shaped" curve. Such a curve for δ measured at 1000 °C is illustrated in Fig. 1 [7].

In the absence of a high concentration of higher-dimensional structural defects such as dislocations and grain boundaries, i.e. at conditions where transport via these defects becomes less important, cation diffusion via point defects may be considered to be most important for the transport of matter. In a material in which one type of point defect predominates, cation transport will occur to a large extent by that point defect species. In the case of magnetite, cation diffusion in the bulk has been found through systematic diffusion studies involving ^{59}Fe tracers to occur by a vacancy mechanism at high oxygen activities and by an interstitialcy diffusion mechanism at low oxygen activities [4, 9]. In addition, as is shown by the slopes of the V-shaped curve in Fig. 2, the oxygen activity dependences of the tracer diffusion coefficient are similar to those of the point defect concentrations which determine the deviation from stoichiometry, δ, in magnetite. In addition, evidence exists that anion bulk diffusion in magnetite is slow in comparison with cation diffusion [10, 11].

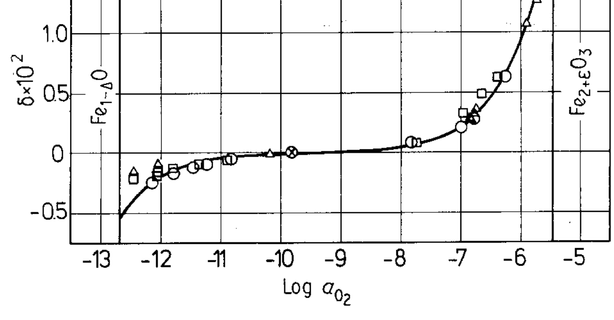

Figure 1 The deviation from stoichiometry, δ, in $Fe_{3-\delta}O_4$ versus oxygen activity for $T = 1000\,°\text{C}$ [7]. (——) Calculated with $K_V = 420$, $K_I = 5 \times 10^{-12}$; experimental data points: (⊗) reference point, (○) sample 1 ($m° = 61.87$ mg), (□) sample 2 ($m° = 126.16$ mg), (△) sample 3 ($m° = 222.8$ mg).

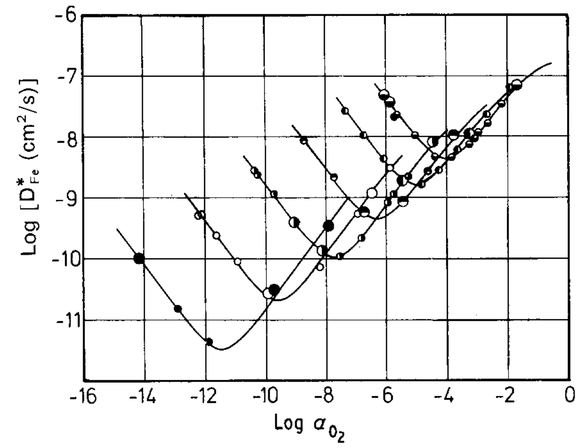

Figure 2 Tracer diffusion coefficients of iron in magnetite as a function of oxygen activity for temperatures ranging from 900 °C to 1400 °C [4]: (◒) 1400 °C, (◐) 1300 °C, (◓) 1200 °C, (◑) 1100 °C, (○) 1000 °C, (●) 900 °C.

3. Cation diffusion-controlled formation of magnetite

By considering the diffusion of iron through a bulk $Fe_{3-\delta}O_4$ product layer, a framework of equations can be developed which may be used to calculate the parabolic rate constant for the formation of magnetite. Such a development exists in [3] and yields an expression for the parabolic rate constant, k_p, in terms of normalized partial cation tracer diffusion coefficients for diffusion via cation vacancies and for diffusion via cation interstitials, Haven ratios for cation diffusion via cation vacancies and cation interstitials, and oxygen activities which correspond to thermodynamic equilibria between Fe and $Fe_{3-\delta}O_4$ and between $Fe_{3-\delta}O_4$ and $Fe_2O_{3-\varepsilon}$. It should be noted, however, that an error exists in the original development; this error (which leads to a numerical inaccuracy of about 15%) is explained in the appendix.

The equation for the parabolic rate constant given in the appendix contains an empirical correction factor for δ in $Fe_{3-\delta}O_4$ which is appropriate for high temperatures and high oxygen activities. For $T < T_{\text{wüs}}$, this correction factor is not needed. Thus, the equation for the parabolic rate constant may be formulated as has been done for the formation of isostructural hausmannite [12]. This equation is given as:

$$k_p = \tfrac{1}{2}(\Delta x)^2/t = 3\xi\{(D^0_{[V]}/f_{[V]})[a''^{2/3}_{O_2} - a'^{2/3}_{O_2}] + (D^0_{[I]}/f_{[I]})[a'^{-2/3}_{O_2} - a''^{-2/3}_{O_2}]\} \qquad (2)$$

where ξ is a stoichiometric coefficient relating the number of moles of $Fe_{3-\delta}O_4$ formed to the number of moles of Fe transported through the bulk product layer, $D^0_{[V]}$ is the partial cation tracer diffusion coefficient for cation diffusion via vacancies normalized to $a_{O_2} = 1$, $D^0_{[I]}$ is the partial cation tracer diffusion coefficient for cation diffusion via cation interstitials normalized to $a_{O_2} = 1$, $f_{[V]}$ ($= 0.56$) is the Haven ratio for cation diffusion via vacancies, $f_{[I]}$ ($= 0.19$) is the Haven ratio for cation diffusion via interstitials, a'_{O_2} is a lower oxygen activity limit (corresponding to the $Fe/Fe_{3-\delta}O_4$ equilibrium here), and a''_{O_2} is an upper oxygen activity limit (corresponding to the $Fe_{3-\delta}O_4/F_2O_{3-\varepsilon}$ equilibrium here). The numerical expressions for evaluating $D^0_{[V]}, D^0_{[I]}, f_{[V]}$, and $f_{[I]}$ as a function of temperature are summarized in Reference 3. The expressions for $\log a_{O_2}(Fe/Fe_{3-\delta}O_4)$ [13] and for $\log a_{O_2}(Fe_{3-\delta}O_4/Fe_2O_{3-\varepsilon})$ [3, 13] as a function of temperature are:

$$\log a_{O_2}(Fe/Fe_{3-\delta}O_4) = -28\,930/T(K) + 8.460 \tag{3}$$

$$\log a_{O_2}(Fe_{3-\delta}O_4/Fe_2O_{3-\varepsilon}) = -24\,660/T(K) + 5.854 + 2.592 \log T(K) \tag{4}$$

4. Interpretation of results

By using the data measured by Gemma *et al.* [2] the parabolic rate constants for the oxidation of pure iron to magnetite have been recalculated according to Equation 1. The results are plotted in Fig. 3. The parabolic rate constants for the oxidation of pure iron to magnetite based on cation bulk diffusion-controlled reaction kinetics have been calculated for the range of temperatures below $T_{\text{wüs}}$ investigated by Gemma *et al.* [2] by using Equation 2 and the numerical expressions for $D^0_{[V]}, D^0_{[I]}, f_{[V]}, f_{[I]}$, $\log a_{O_2}(Fe/Fe_{3-\delta}O_4)$, and $\log a_{O_2}(Fe_{3-\delta}O_4/Fe_2O_{3-\varepsilon})$ given in References 3 and 13. The results of these calculations also appear in Fig. 3.

As shown in Fig. 3, the rate constants calculated by using Equation 2 are as much as two orders of magnitude smaller than the rate constants calculated by using the experimental data of Gemma *et al.* [2]. It may be concluded from these results that the role of cation bulk diffusion in the formation of magnetite is small; this assumes of course that the data collected by Gemma *et al.* [2] have been measured precisely. In addition, the gap between the experimental results and the calculated data, as shown in Fig. 3, decreases with increasing temperature suggesting that the contribution from cation bulk diffusion to the overall reaction kinetics decreases with decreasing temperature.

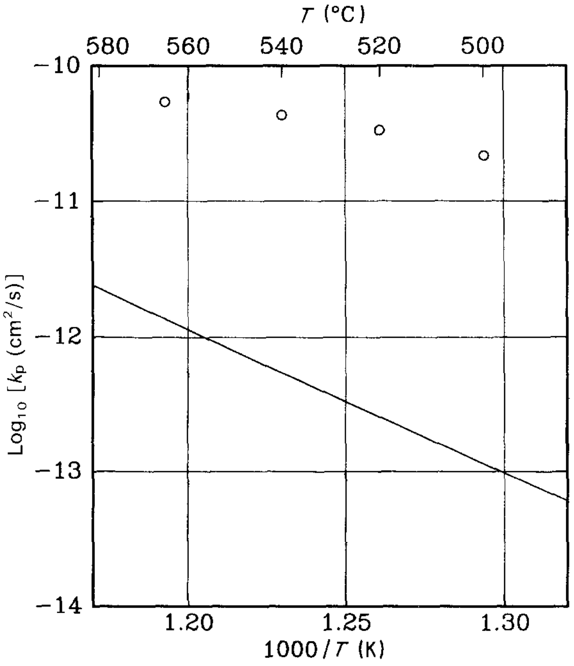

Figure 3 $\log_{10} k_p$ versus $1000/T$ for the data of Gemma *et al.* (○) [2] and for the data calculated based on cation bulk diffusion-controlled reaction kinetics (——).

It is dangerous, in general, to speculate on the mechanism of diffusion which is rate controlling in this case. While it is safe to assume from the results in Fig. 3 that cation diffusion in the bulk of the product layer contributes only slightly to the overall reaction kinetics, one can only guess at other mechanisms which contribute to the oxidation. In a relatively old and at least partly outdated paper, Davis *et al.* [14] have suggested that the growth of magnetite on wüstite is due to a large extent to the transport of oxygen ions. Based on this paper, Gemma *et al.* [2] speculate that this may also be the case in the oxidation of pure iron to magnetite. However, based on the cation and anion diffusion data known for magnetite, this cannot be the case if bulk diffusion prevails. A much more reasonable explanation for the fact that the rate constants measured by Gemma *et al.* [2] are so much larger than the rate constants which may be expected based on cation bulk diffusion-controlled reaction kinetics is that there are very significant contributions to the overall reaction kinetics from the transport of iron and/or oxygen along grain boundaries and/or dislocations.

Any further statement on the overall reaction kinetics would require a much more extensive analysis of the transport mechanisms involved in the oxidation reaction than has been considered in Reference 2. For example, Atkinson has systematically investigated the contributions of transport along dislocations and of transport along grain boundaries to the kinetics of the oxidation of nickel [15]. Only after a comprehensive study such as this can one begin to quantitatively attribute the extent of particular transport mechanisms to an overall oxidation reaction process.

Appendix

The error in the development of the equation for the parabolic rate constant in Reference 3 arises from the integration of Equation 14 in that paper. The resulting expression in Equation 15 should be:

$$j_{Fe} = \frac{3}{\Delta x V^m}\left\{\frac{A}{2K_V}\ln\left[\frac{1 + 2K_V a''^{2/3}_{O_2}}{1 + 2K_V a'^{2/3}_{O_2}}\right] + B\left[a'^{-2/3}_{O_2} - a''^{-2/3}_{O_2}\right]\right\} \tag{5}$$

where Δx is the thickness of the magnetite product layer, K_V is an equilibrium constant for the formation of cation vacancies, V^m is the molar volume of $Fe_{3-\delta}O_4$, a'_{O_2} is a lower oxygen activity limit (as given for Equation 2), and a''_{O_2} is an upper oxygen activity limit. A and B are coefficients containing normalized partial tracer diffusion coefficients and Haven ratios for cation diffusion by vacancies and interstitials, respectively [3]. The error is carried through to the final result given by Equation 17 which should read:

$$k_p = \tfrac{1}{2}(\Delta x)^2/t = 3\xi\left\{\left[\frac{A}{2K_V}\right]\ln\left[\frac{1 + 2K_V a''^{2/3}_{O_2}}{1 + 2K_V a'^{2/3}_{O_2}}\right] + B\left[a'^{-2/3}_{O_2} - a''^{-2/3}_{O_2}\right]\right\} \tag{6}$$

where ξ is a stoichiometric coefficient relating the number of moles of $Fe_{3-\delta}O_4$ formed to the number of moles of Fe transported through the bulk product layer. Empirical expressions as a function of T for K_V, $D^0_{[V]}$ (contained in A), and other relevant parameters are summarized in Reference 3. The differences between the correct result given above and the erroneous equation in Reference 3 are that instead of using the natural logarithm ("ln"), the base ten logarithm ("log") has been used in Reference 3 and a factor of two in the denominator of the coefficient which also contains A in Equation 6 is missing in Reference 3. This leads to a numerical error of the order of 15% in calculations performed with the equation originally reported in Reference 3.

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