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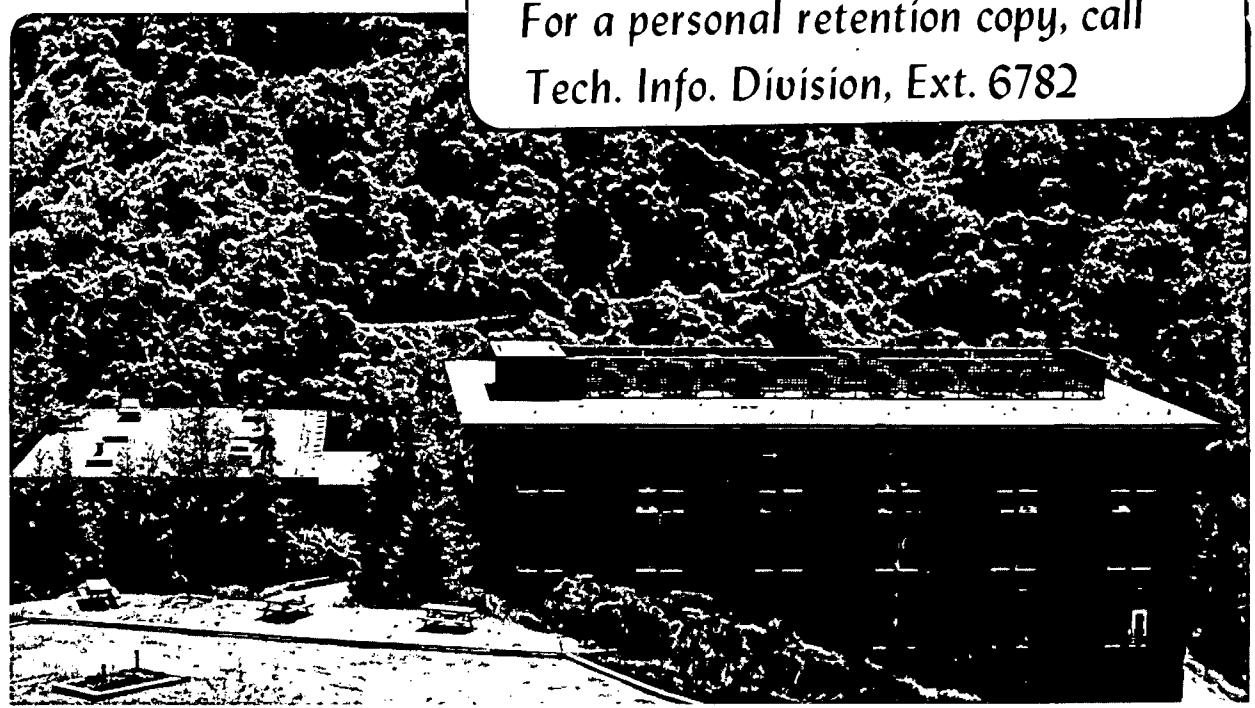
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THE REACTION INTERFACE IN REDUCTION

Mei Chang and Lutgard C. De Jonghe

July 1980

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INTRODUCTION

When an oxide such as cobalt ferrite is reacted with hydrogen, a porous metal scale will form topochemically from its surface. The pores in the metal scale permit the reducing gas to reach the reaction interface directly. At the pore bottoms the parent oxide is then destroyed by the reduction process, the oxygen is removed in the form of water vapor, and the cations that are produced at the pore bottoms are transported to the adjacent metal phase. The purpose of the present paper is to clarify the processes occurring at the metal/oxide reaction interface, and to determine which sub-processes are most important in determining the interface reaction rates.

Gaseous reduction of oxides can be considered to occur in three steps: 1. External mass transfer, 2. Gas transport through the porous product scale, and 3. Chemical reaction at the interface. Under conditions of sufficient gas flow at the specimen, the mass transfer step may be ignored. For reduction of a semi-infinite flat slab by pure hydrogen, the reduction kinetics for a simple topochemical reaction in which there is a phase sequence of unreduced oxide/porous metal scale, a simple kinetic equation prevails [1,2]

$$J^{-1} = C_{H_2}^o \left(\frac{\xi}{D_{eff}} + \frac{1}{k_r} \right)^{-1} \quad \text{Eqn. 1}$$

where J = the rate of reduction; $C_{H_2}^0$ = the hydrogen concentration at the specimen surface; R = gas constant; T = absolute temperature; D_{eff} = effective gas diffusivity in the porous product scale; k_r = interface reaction parameter. From an analysis of thermogravimetric data of oxide reduction it is then possible to determine D_{eff} and k_r from the slope and intercept of a J^{-1} versus ξ plot, provided Eqn. 1 is valid. Porter and De Jonghe established the validity of Eqn. 1 for cobalt ferrite [2] below 650°C , and proposed an interface reaction such as the one briefly condensed by Wagner [3]. Wagner, however, appeared to rule out solid state diffusion control on the basis that the reaction interface is near equilibrium. In this work we cannot adopt this assumption. An analysis was performed of k_r as a function of $p_{H_2}^0$ and T , for cobalt ferrite reduced by hydrogen in the temperature range of 560° to 620°C and in $p_{H_2}^0$ range at 50 to 250 torr. This analysis yielded information on the nature of the reactions occurring at the oxide/scale interface.

EXPERIMENTAL

The reduction kinetics of cobalt ferrite by hydrogen were determined thermogravimetrically. The details of the method have been described previously [2]. The oxide was 99% dense, with a grain size of about 10 micron. The hydrogen gas had a controlled H_2O content of 100 ppm. Gas flow rates were such that the external mass transfer resistance could be neglected.

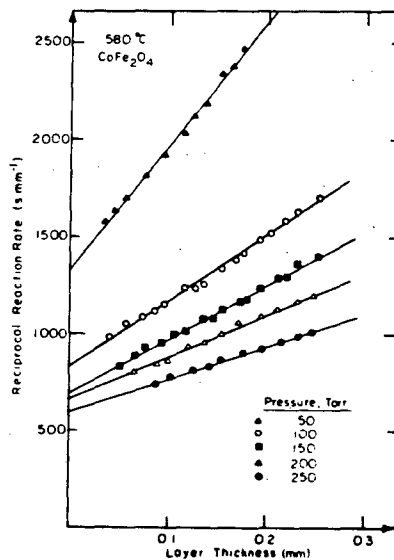


Fig. 1. Reduction kinetics at 580°C . Reciprocal interface advance rate versus layer thickness

RESULTS AND DISCUSSIONS

Eqn. (1) indicates that a linear relationship should be observed between ξ^{-1} and ξ . The experimental data indeed show this, as is clear from Figure 1 for a variety of pressures at 580°C. From data such as these D_{eff} and k_r could be obtained.

It was shown by Porter and De Jonghe [2] that the reaction occurring at the oxide/metal interface, described by the parameter k_r , followed Langmuir-Hinshelwood kinetics for the hydrogen reduction of cobalt ferrite under the conditions of interest here. Thus, k_r may be written as:

$$k_r^{-1} = A_1 + A_2 C_{\text{H}_2}^b \quad \text{Eqn. 2}$$

where A_1 and A_2 are rate parameters, and $C_{\text{H}_2}^0 = p_{\text{H}_2}^0 / RT$. k_r relates the reaction rate J and the hydrogen concentration at the interface. The hydrogen concentration at the interface $C_{\text{H}_2}^i = C_{\text{H}_2}^0$ when the layer thickness $\xi = 0$. Thus, $J = k_r C_{\text{H}_2}^0$. Figure 2 shows that the

reciprocal of the interface reaction rate parameter k_r is proportional to hydrogen bulk pressure. From these data the values of A_1 and A_2 can be obtained. The values of A_1^{-1} and A_2^{-1} have been plotted in Figure 3, and their activation enthalpies has been

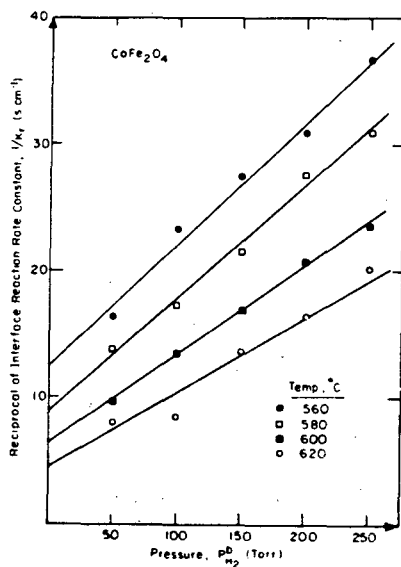


Fig. 2. Reciprocal interface reaction rate parameters as a function of bulk hydrogen pressure. Langmuir-Hinshelwood kinetics are obeyed.

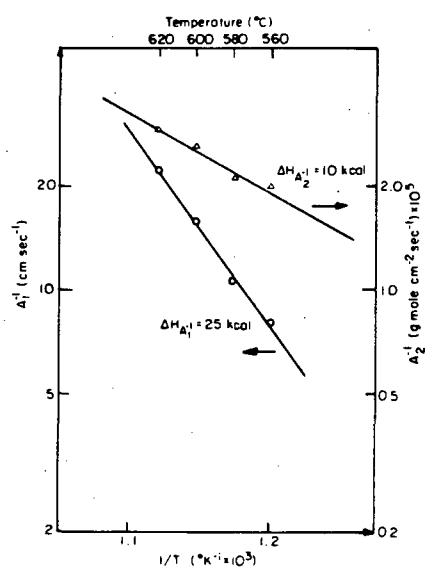
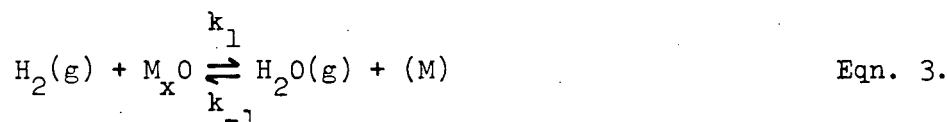


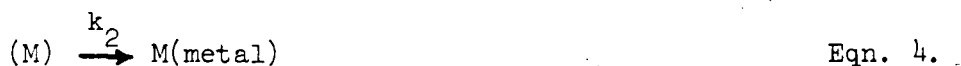
Fig. 3. Arrhenius plot for the Langmuir-Hinshelwood rate constants A_1^{-1} and A_2^{-1} . The activation enthalpies are indicated in kcal/mole.

indicated. These activation energies were 10 and 25 kcal/mole for A_1^{-1} , and A_2^{-1} respectively. A variety of interface reaction models can be constructed that all lead to the same functional relationship between k_r and p_{H_2} . The distinction between the various mechanisms has to come from the temperature dependence of A_1 and A_2 . As was discussed by Porter and De Jonghe (2), a solid state diffusion process must occur at the reaction interface to permit the continued development of the reaction product scale. The essential aspects of the near interface solid state transport are that the excess cations, generated at the pore bottoms diffuse to the adjacent metal phase, while at the same time oxygen ions diffuse from under the advancing metal to the pore bottoms. The anion transport is required to permit the uniform advancing of the interface. No external shape change was observed in the reduction of the oxide to metal, indicating that the rate of metal/oxide interface anion transport was sufficiently high as to permit the metal/oxide interface to keep pace with the advancing gas/oxide interface at the pore bottom. It can then be assumed that the entire solid state process is controlled by the transport of excess cations that are produced at the pore bottom.

Although the interface reaction appears to be quite complex, a number of possibilities can be ruled out. From the catalysis literature it seems well established that at the temperatures of interest in this study catalytic effects are no longer significant [4]. Further, competitive adsorption of water vapor and hydrogen should no longer occur, and water desorption is expected to be very rapid on oxides, such as CoFe_2O_4 , that do not contain dissolved hydroxyl groups. The gas/solid reaction can then simply be described by the chemical equation:



Such a reaction does not lead to a Langmuir-Hinshelwood relationship for the pressure dependence of the reaction rate. It is only when competitive adsorption occurs (which could be ruled out), or when the solid state transport step is taken into account that Langmuir-Hinshelwood kinetics are obtained. The solid state transport step can be chemically symbolized as:



where (M) now is the concentration of excess cation-electron groups generated at the pore bottom and $J = k_1(\text{M})$ is a statement of Fick's law. Thus, at $\xi = 0$ where $J = k_r C_{\text{H}_2}^{\text{O}}$ and where $C_{\text{H}_2\text{O}}^{\text{O}} \approx 0$, we find:

$$k_r^{-1} = 1/k_1 + C_{\text{H}_2}^{\text{O}}/k_2 \quad \text{Eqn. 5.}$$

k_2 thus describes the rate of the solid state cation transport from the pore bottom to the metal phase.

It should be noted that an identical argument could have been made considering the transport of oxygen at the metal-oxide interface. The conclusions concerning the solid state transport path of the ions thus apply to either oxygen or cations.

This solid state diffusion step could involve interface diffusion or volume diffusion. From the observations of Porter and De Jonghe [2] on the reaction interface morphology, it appears that these diffusion processes occur in geometrical conditions analogous to those of cellular growth [5]. If the pore spacing is λ , then we expect for the reaction rate R

$$R \propto D_v/\lambda - \text{volume diffusion} \quad \text{Eqn. 6}$$

$$R \propto D_s/\lambda^2 - \text{Interface diffusion} \quad \text{Eqn. 7}$$

Where D_v is the volume diffusive coefficient and D_s the interface diffusion coefficient of the excess cations. We thus expect

$k_2\lambda \propto D_s$ for volume diffusion and $k_2\lambda^2 \propto D_s$ for interface diffusion.

In the temperature and pressure range studied here, the interface pore spacing λ was found to increase only marginally with temperature; the activation energy describing the temperature dependence of λ was found to be around +5kcal/mole. This would lead to the possibility of an activation enthalpy of about 15kcal/mole for D_v , and about 20 kcal/mole for D_s . The value for volume diffusion cannot be reconciled with expected cation volume diffusion activation enthalpies of about 30 to 60 kcal/mole. The activation energy for D_s is, however, quite plausible. It is therefore concluded that the interface reaction is controlled by a gas-oxide reaction at the pore bottom, coupled with interface diffusion of the generated excess cations to the metal phase and of the oxygen to the pore bottoms.

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