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Diffusion in Polycrystalline Magnesiowüstite Determined by Reduction Kinetics

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Polycrystalline magnesiowüstite samples (5 wt% Fe_2O_3 doped) were reduced (or oxidized) at various temperatures in CO_2–CO gas mixtures and N_2–O_2 gas mixtures. The reaction was followed continuously with a Cahn microbalance. The kinetics in the high oxygen partial pressure region (0.18–9.6×10^{-6} atm) were controlled by cation vacancy diffusion. The chemical diffusion coefficient of iron in magnesiowüstite was found to increase linearly with the concentration of cation vacancies. The activation energy for diffusion was found to be 45 kcal/mol.

The pseudochemical diffusion coefficient of iron in magnesiowüstite evaluated from the kinetics of reduction and oxidation in low oxygen partial pressure atmospheres (10^{-7}–10^{-10} atm) was found to decrease as the concentration of cation vacancies increased. The reduction kinetics could be interpreted best by assuming an initial desorption of oxygen on the surface of the solid solution, and the migration of oxygen away from the grain boundaries of the sample followed by an associated solid state diffusion process.

Introduction

Systematic investigations of the system, MgO–FeO–Fe_2O_3, were carried out by Richards and White (*1*) and Woodhouse and White (*2*). Subsequently the system was studied by Paladino (*3*); Phillips, Sonniya, and Maun (*4*); Reihnen (*5*); and recently by Speidel (*6*) and Whillshee and White (*7*). The oxidation-reduction equilibria in mangesiowüstite determined by Brynestad and Flood (*8*) revealed that Fe^{3+} ions were associated with cation vacancies. A recent work by Alcock and Iyengar (*9*) with dilute Fe_xO in MgO disclosed a region at low oxygen partial pressure where the Fe^{3+}/Fe^{2+} ratio was independent of P_{O_2}.

Rigby and Cutler (*10*) established a relationship between the concentration of cation vacancies and diffusion coefficients in the Fe_xO–MgO system in air. They noted that the diffusivity varied approximately exponentially with cation vacancy concentration. The enthalpy of activation for diffusion reaction, 47.5 kcal/mol, remained independent of vacancy concentration. Blank and Pask (*11*) found that the activation energy of the Fe–MgO system increased from 29.6–43.5 kcal/mol in vacuum with an increase of 5–20% at. % of iron.

The chemical diffusion coefficient of cations in the wüstite phase has been investigated thermogravimetrically by reduction of wüstite both in CO_2–CO and H_2–H_2O mixtures. Levin and Wagner (*12*) determined the diffusivity of iron in wüstite by reduction of wüstite in CO_2–CO gas mixtures over the temperature range 900–1100°C. They found that cation diffusivities decrease as the cation vacancy concentration increases. The activation energy was also a function of composition and ranged from 24.8–37.4 kcal/mol.

The same system was studied by Landler and Komarek (*13*) by using H_2–H_2O mixtures as the reducing atmosphere. They believed the reactions were controlled by a combined surface reaction plus solid state diffusion process. The surface reaction constant was calculated independently from the initial slope of the experimental weight change curves. The surface rate constant was found to be proportional to the iron vacancy concentration at the wüstite surface. The chemical diffusion coefficient was also found to decrease with increasing vacancy concentration. Both Levin and Landler proposed a qualitative explanation of their results by assuming a lower of the mobility of iron vacancies due to repulsive interaction.

Presently Hembree and Wagner (*14*) measured the iron tracer diffusion coefficient in wüstite at 1100°C. The equation is $D = 3 \times 10^{-29}\,[V''_{Fe}]$ where

$[V''_{Fe}]$ denotes the concentration of vacancies in number/cm^3. Thus the explanation of Levin and Landler is no longer valid.

Magnesiowüstite loses weight when the oxygen partial pressure is lower than its previous equilibrium value at a constant temperature. Increasing the temperature at same oxygen partial pressure will also result in a weight loss. This is illustrated with the equation

$$O_O + 2Fe^{\cdot}_{Mg} + V''_{Mg} \rightleftarrows \tfrac{1}{2}O_2(g) + 2Fe_{Mg}, \quad (1)$$

where

Fe_{Mg} = ferrous iron on a regular cation site;

$Fe^{\cdot}_{Mg}$ = positive hole (Fe^{3+} ion on a regular cation site),

V''_{Mg} = cation vacancy,

O_O = oxygen ion on an anion site.

A study of diffusion in a dilute Fe_xO–MgO solid solution by reduction and oxidation has many advantages over similar studies in wüstite. The vacancy concentration is more dilute with a smaller possibility of interaction. Most important is the fact that the solid solution is stable over a very broad range of oxygen partial pressures.

Experimental Method

Fisher's electronic grade MgO powder (particle size 99.5% less than 20 nm) was mixed with reagent grade Fe_2O_3 and isopropanol in a ball mill for 6 hr. The mixed material was dried, crushed, passed through an 80 mesh screen, and calcined at 900°C. The prepared powder mixtures were pressed at 20000 psi into 1-in. pellets using distilled water as a binder. The pellets were fired at 1650°C in a gas furnace for 5 hr. They were then annealed at the desired working temperature for at least 2 days. The resulting open porosity was less than 1% as determined by liquid absorption. The prepared sample had a diam. of 2.1 cm and 0.136–0.168 cm thick. Their weight varied between 1.4706 g and 1.9272 g. The average grain size was determined to be approximately 37 μm.

The ferric and ferrous ion contents in the solid solution were determined by the colorimetric method from samples dissolved under CO_2 gas atmosphere by using degassed, concentrated hydrochloric acid. Details of this analysis were described by Alcock (*9*).

A molybdenum wound, hydrogen atmosphere furnace with a $1\frac{1}{4}$ in. diam. closed-end mullite tube was used in thermogravimetric studies. The temperature was controlled within ±2°C. The weight changes were recorded by using a Cahn RG Micro balance.

For high oxygen partial pressure atmospheres, N_2–O_2 gas mixtures were used to establish the desired P_{O_2}; in low P_{O_2} atmospheres, the partial pressure of oxygen was controlled by mixing CO_2 and CO gases in different proportions. The CO_2 was purified by passing through activated alumina. The mixed gases were allowed to flow to the air for at least 30 min before being admitted into the furnace in order to flush the whole gas controlled system and to check the stability of the flowmeters. A flow rate of 6 cm^3/sec was used in all of the kinetic studies. The kinetics of weight change were checked against a H_2–H_2O gas system and found to be within experimental error for one temperature and partial pressure of oxygen.

Equilibrium Data

The stoichiometry of magnesiowüstite as a function of P_{O_2} and temperature can be calculated from the equilibrium weight change data. Magnesiowüstite (5 wt% Fe_2O_3) at 1200°C and air atmosphere was used as a reference composition, the Fe^{3+}/Fe^{2+} ratio was determined from a furnace cooled sample. The ratio of Fe^{3+}/Fe^{2+} from chemical analysis was 32.15. Assuming that the concentration of vacancies is equal to one half the concentration of the ferric ions, the stoichiometry of 5 wt% Fe_2O_3 doped magnesiowüstite can be generated from this reference composition. The results are in good agreement with the data of Alcock (*9*).

Reductions and Oxidations of Magnesiowüstite in High Oxygen Partial Pressure Atmospheres

Thermogravimetric measurements for magnesiowüstite (5 wt% Fe_2O_3) at high P_{O_2} atmospheres were conducted at $P_{O_2} = 1.64 \times 10^{-2}$ atm and 9.6×10^{-6} atm, respectively. The square of the weight loss per unit geometric surface area versus time plots (Figs. 1 and 2) revealed that the reduction reaction follows a parabolic rate equation. The oxidation kinetics in air back to the original weight also followed a parabolic law. However, oxidation at 1380 and 1420°C between $P_{O_2} = 9.6 \times 10^{-6}$ atm and air atmosphere was not exactly parabolic. In this region of oxygen partial pressure the rate of oxidation was always larger than the rate of reduction at all temperatures.

The parabolic rate constant, k_p, was calculated from the slope of the lines in Fig. 1 and 2. The relation between the parabolic rate constant and the

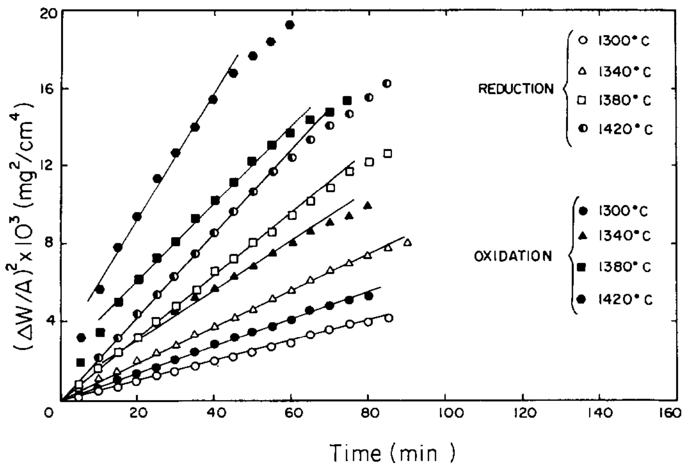

FIG. 1. Parabolic rate curves for reduction and oxidation of magnesiowüstite between $P_{O_2} = 0.18$ and 0.0164 atm.

chemical diffusion coefficient for diffusion in or out of a thin slab is well-known (*12*). When $\tilde{D}t/l^2 < 0.15$, the chemical diffusion coefficient in magnesiowüstite can be evaluated from the equation

$$\tilde{D} = \frac{\pi}{4}\left(\frac{k_p}{(\Delta W_e)^2}\right), \qquad (2)$$

where

k_p = parabolic rate constant,

ΔW_e = the total weight change per unit volume after the sample reaches its new equilibrium with the gas atmosphere,

l = the half thickness of the magnesiowüstite,

provided that the assumption that the surface concentration is always in equilibrium with the atmosphere.

The diffusivity can also be obtained by solving Fick's second law of diffusion, using the separation of variables method (*15*). The solutions are denoted as $\tilde{D}_l$; for values of $\tilde{D}_l t/l \geqslant 0.30$ we have

$$\log\left(1 - \frac{\Delta W}{\Delta W_e}\right) = \frac{\pi^2 \tilde{D}_l t}{2.303(4l^2)} + \log\left(\frac{8}{\pi^2}\right); \qquad (3)$$

where $\Delta W/\Delta W_e$ = fractional amount removed at any time t.

Both error function (Eq. 2) and separated variable (Eq. 3) solutions require instantaneous change of vacancy concentration on the surface of the sample. This can be judged from the parabolic plot: If the reduction fits this criterion, the extrapolations of the straight part of the parabolic plot will have an intercept on the ordinate (weight loss squared scale) or go through the origin. In this case the $\tilde{D}$ and $\tilde{D}_l$

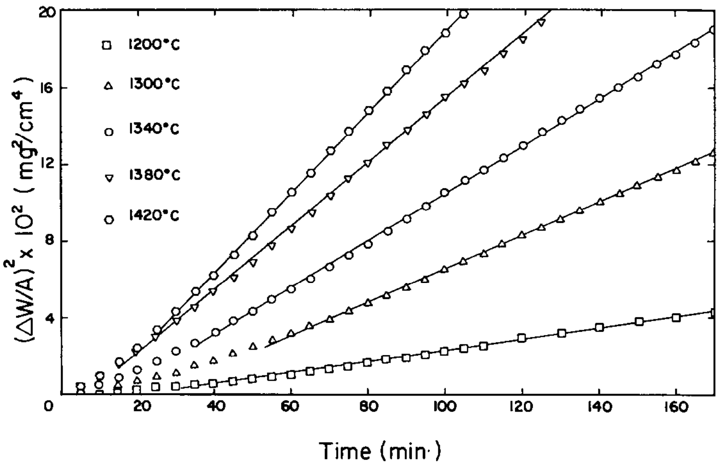

FIG. 2. Parabolic rate curves for reduction of magnesiowüstite between $P_{O_2} = 0.18$ and 9.6×10^{-6} atm.

TABLE I

APPROXIMATE TIME REQUIRED TO REACH THE NEW EQUILIBRIUM IN REDUCTION AND OXIDATION OF MAGNESIOWÜSTITE (5 wt% Fe_2O_3)

air $\rightleftarrows P_{O_2} = 9.6 \times 10^{-6}$ atm

T (°C)	Reduction	Oxidation
1200	24 hr	14 hr
1300	23 hr	6 hr
1340	20 hr	—
1380	16 hr	5 hr
1420	11 hr	—

air $\rightleftarrows P_{O_2}$ at 1200°C

P_{O_2} (atm)	Reduction	Oxidation
10^{-10}	50 min	270 min
10^{-9}	120 min	290 min
10^{-8}	410 min	250 min

agree remarkably well (Table II, reductions from air to $P_{O_2} = 0.016$ atm).

In case of extrapolation of the parabolic plot that has an intercept on the abscissa (time scale), this would indicate that the surface needs time to reach its new equilibrium conditions. Because a finite amount of time will always be needed for the surface to reach its new equilibrium concentration, the boundary condition of zero time can only be approached. If the induction period is short when compared to the total time required to reach its new equilibrium, then the assumption that the boundary conditions are satisfied for the calculations of chemical diffusivity is reasonable.

The resulting $\tilde{D}_l$ and $\tilde{D}$ values are listed in Tables II and III. The fraction of vacant cation sites, N_v, calculated from the equilibrium data is also listed in the tables. The values of $\tilde{D}$ and $\tilde{D}_l$ are in good agreement within the precision of the data indicating that diffusion is indeed the process responsible for the rate of weight change.

The diffusivity via Eq. (2) was evaluated from the isobaric thermogravimetrical studies in addition to isothermal studies. The magnesiowüstite samples were equilibrated at 1200°C with $P_{O_2} = 0.0164$ atm or at 0.18 atm (air); the temperature was then rapidly raised (within 5 min) to 1265, 1300, 1340, 1380, and 1420°C, respectively. The weight loss data recorded as a function of time followed a parabolic law. The surface concentration of vacancies at the surface is the concentration at the higher temperature. The results are listed in Tables IV and V.

In oxidation, the addition of oxygen on the sample surface will create more vacancies on or near the surface than in the bulk. The cations move easier toward the surface in this case than during reduction; hence, the diffusivities obtained from the oxidation kinetics are always greater than those of reduction.

The relationship between the chemical diffusivity and cation vacancy concentrations can be estab-

TABLE II

VALUES OF THE PARABOLIC RATE CONSTANT, k_p, AND THE CHEMICAL DIFFUSION COEFFICIENT FROM THE INITIAL ($\tilde{D}$) AND LATER STAGES ($\tilde{D}_l$) REDUCTION OF MAGNESIOWÜSTITE (5 wt% Fe_2O_3)

T (°C)	k_p (mg^2/cm^4 sec)	$\tilde{D}$ (cm^2/sec)	$\tilde{D}_l$ (cm^2/sec)	N_v at T°C and P_{O_2}
		air $\rightarrow P_{O_2} = 0.0164$ atm		
1300	9.0×10^{-7}	2.15×10^{-7}	2.01×10^{-7}	1.015×10^{-2}
1340	1.52×10^{-6}	2.86×10^{-7}	3.0×10^{-7}	0.969×10^{-2}
1380	2.72×10^{-6}	4.15×10^{-7}	4.25×10^{-7}	0.91×10^{-2}
1420	3.57×10^{-6}	4.5×10^{-7}	4.65×10^{-7}	0.86×10^{-2}
		air $\rightarrow P_{O_2} = 9.6 \times 10^{-6}$ atm		
1200	5.04×10^{-6}	0.91×10^{-7}	1.3×10^{-7}	0.735×10^{-2}
1300	1.42×10^{-5}	1.61×10^{-7}	1.9×10^{-7}	0.511×10^{-2}
1340	2.08×10^{-5}	1.64×10^{-7}	1.98×10^{-7}	0.348×10^{-2}
1380	2.9×10^{-5}	1.73×10^{-7}	2.05×10^{-7}	0.188×10^{-2}
1420	9.96×10^{-5}	1.54×10^{-7}	1.8×10^{-7}	0.0177×10^{-2}

TABLE III

VALUES OF THE PARABOLIC RATE CONSTANT, k_p, AND THE CHEMICAL DIFFUSION COEFFICIENTS, $\tilde{D}$, FROM THE INITIAL STAGES OF OXIDATION OF MAGNESIOWÜSTITE (5 wt% Fe_2O_3)

T (°C)	k_p (mg²/cm⁴ sec)	$\tilde{D}$ (cm²/sec)	N_v at T°C and air
	$P_{O_2} = 0.0164$ atm → air		
1300	1.19×10^{-6}	2.82×10^{-7}	1.156×10^{-2}
1340	2.37×10^{-6}	3.64×10^{-7}	1.126×10^{-2}
1380	3.37×10^{-6}	5.26×10^{-7}	1.079×10^{-2}
1420	5.9×10^{-6}	7.2×10^{-7}	1.048×10^{-2}
	$P_{O_2} = 9.6 \times 10^{-6}$ atm → air		
1200	8.3×10^{-6}	1.49×10^{-7}	1.25×10^{-2}
1300	4.15×10^{-5}	4.7×10^{-7}	1.156×10^{-6}
1380	not parabolic		1.079×10^{-2}
1420	not parabolic		1.048×10^{-2}

TABLE IV

VALUES OF THE PARABOLIC RATE CONSTANT, k_p, AND THE CHEMICAL DIFFUSION COEFFICIENTS, $\tilde{D}$, FROM THE INITIAL STAGES OF REDUCTION OF MAGNESIOWÜSTITE BY INCREASING THE TEMPERATURE FROM 1200 → T°C AT $P_{O_2} = 0.18$ atm

T°C	k_p (mg²/cm⁴ sec)	$\tilde{D}$ (cm²/sec)	N_v at T°C and $P_{O_2} = 0.18$ atm
1300	8.71×10^{-7}	5.16×10^{-7}	1.156×10^{-2}
1340	3.0×10^{-6}	9.85×10^{-7}	1.126×10^{-2}
1380	7.61×10^{-6}	1.3×10^{-6}	1.079×10^{-2}
1420	3.87×10^{-5}	4.76×10^{-6}	1.048×10^{-2}

lished by the help of projecting the reduction diffusivities in the high P_{O_2} region onto a single temperature, say 1200°C, assuming a simple Arrhenuis Law. The 47.5 kcal/mol was used as the activation energy of the reaction based on Rigby's data. The results are shown in Fig. 3. These diffusivities represent the different values of $\tilde{D}$ as if they were obtained at different vacancy concentrations at 1200°C. An approximate linear relation exists between $\tilde{D}$ and cation vacancy concentration.

At best this linear relation is only an approximation and cannot fit the data exactly because in all experiments the diffusion coefficient is a function of concentration of vacancies and Eqs. (2) and (3) assume that $\tilde{D}$ is not a function of concentration of vacancies (depth into the sample). The parabolic solution is expected to represent the reduction data better than oxidation. During reduction, diffusion is controlled by a low vacancy concentration region near the surface. Even these data scatter when the

TABLE V

VALUES OF THE PARABOLIC RATE CONSTANT, k_p, AND THE CHEMICAL DIFFUSION COEFFICIENTS, $\tilde{D}$, FROM THE INITIAL STAGES OF REDUCTION OF MAGNESIOWÜSTITE BY INCREASING THE TEMPERATURE FROM 1200 → T°C ($P_{O_2} = 0.0164$ atm)

T (°C)	k_p (mg²/cm⁴ sec)	$\tilde{D}$ (cm²/sec)	N_v at T°C and $P_{O_2} = 0.0164$ atm
1265	3.22×10^{-7}	1.9×10^{-7}	1.062×10^{-2}
1300	1.60×10^{-6}	3.6×10^{-7}	1.015×10^{-2}
1340	3.83×10^{-6}	4.66×10^{-7}	0.967×10^{-2}

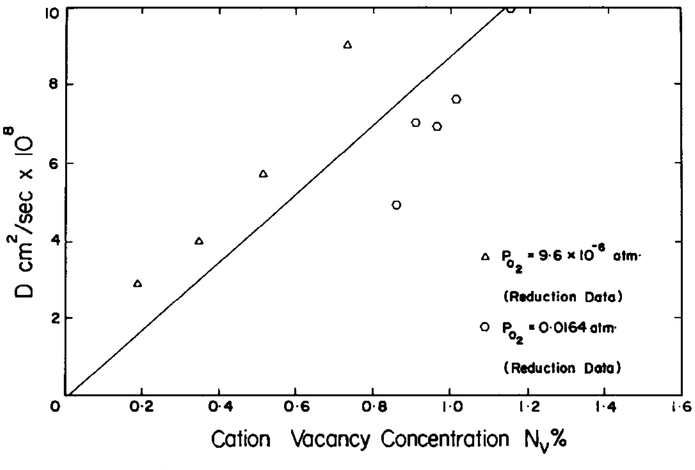

FIG. 3. Chemical diffusion coefficient of iron in magnesiowüstite as function of cation vacancy concentration in N_v by projecting different values of $\tilde{D}$ on to 1200°C isothermal.

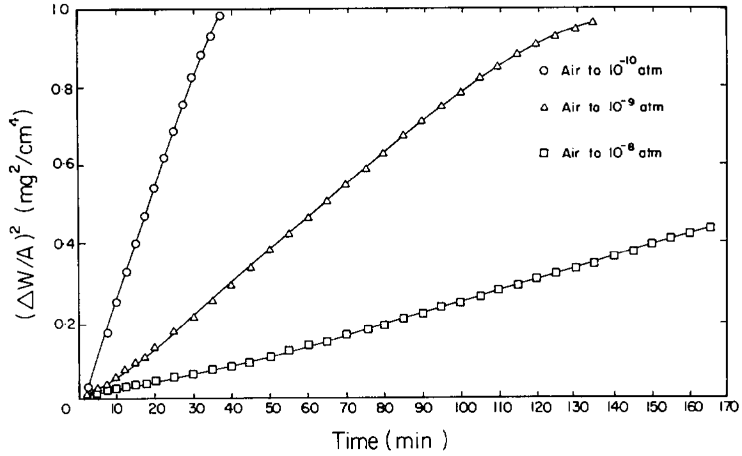

FIG. 4. Parabolic rate curves for reduction of magnesiowüstite at 1200°C.

driving force is high (large difference in P_{O_2} or temperature).

Reduction and Oxidation of Magnesiowüstite in Low Oxygen Pressure Atmospheres

In this partial pressure range, the reduction reaction was very fast. Both reduction and oxidation kinetics followed the parabolic rate equation at 1200°C. Although the reduction kinetics obeyed the parabolic reaction law at 1250°C, the oxidation kinetics were not parabolic. When the temperature was increased to 1300°C, the parabolic equation failed completely to represent either reduction or oxidation. Representative data are shown in Fig. 4 for 1200°C.

In the low P_{O_2} atmospheres, the oxidation and reduction of magnesiowüstite had the following characteristics:

(a) A very rapid, almost linear initial rate was observed in all oxidation and the reduction curves (see Fig. 5).

(b) The reduction rate increases as P_{O_2} decreases.

(c) A sudden change of the curvature of the rate curves within the first 5 min was observed in both the reduction and oxidation experiments.

(d) At low temperatures the reduction process follows parabolic rate equation as well.

(e) Except at $P_{O_2} = 10^{-8}$ atm, the reduction kinetics are faster than the oxidation kinetics (Table I).

(f) The rate of oxidation was nearly the same regardless of the previous reduction but the initial intercept or "non" diffusion controlled sections were greater for the lower P_{O_2} previous reduction.

The calculated chemical diffusivities are listed in Table VI. Since these are only indicative of the reduction reaction at low temperatures, it must be kept in mind that the reduction proceeds very fast indeed at temperatures of 1300–1400°C.

The chemical diffusivities of iron in magnesiowüstite obtained from the reduction kinetics are plotted in Fig. 6 as function of P_{O_2}. Since the cation vacancy concentration decreases as the P_{O_2} decreases, it appears that the D increases with increas-

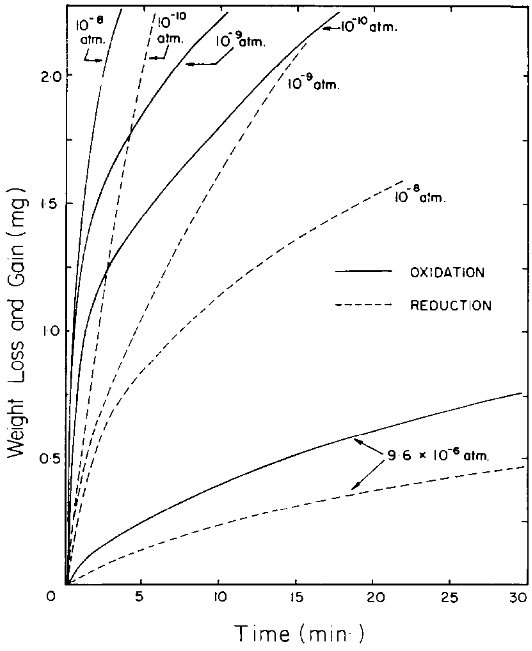

FIG. 5. Initial weight change rate curves for reduction and oxidation of magnesiowüstite in between $P_{O_2} = 0.18$ atm and P_{O_2} as indicated at 1200°C.

TABLE VI

VALUES OF THE PARABOLIC RATE CONSTANT, k_p, AND THE CHEMICAL DIFFUSION COEFFICIENTS, $\tilde{D}$, FROM INITIAL STAGES OF REDUCTION AND OXIDATION OF MAGNESIOWÜSTITE ($T = 1200°C$)

P_{O_2} (atm)	k_p (mg²/cm⁴ sec)	$\tilde{D}$ (cm²/sec)	N_v at P_{O_2}
	Reduction data		
10^{-10}	7.1×10^{-4}	2.42×10^{-6}	0.0262×10^{-2}
10^{-9}	1.42×10^{-4}	5.1×10^{-7}	0.063×10^{-2}
10^{-8}	5.05×10^{-5}	1.72×10^{-7}	0.108×10^{-2}
	Oxidation data		
10^{-10}	1.08×10^{-4}	3.7×10^{-7}	1.25×10^{-2}
10^{-9}	8.92×10^{-5}	3.22×10^{-7}	1.25×10^{-2}
10^{-8}	1.13×10^{-5}	4.4×10^{-7}	1.25×10^{-2}

ing vacancy concentration in the high P_{O_2} atmospheres and increases with decreasing cation vacancy concentration in the low P_{O_2} atmospheres.

A study of a granular sample provided some information about the reduction kinetics of magnesiowüstite at low P_{O_2}. The grain size of 5 wt% Fe_2O_3 doped pellet was determined to be approximately 37 μm. Sintered pellets were crushed into approximately 35 μm particles. The powder was then placed into an alumina crucible. The kinetics of reduction was studied at 1200°C and several different oxygen partial pressure. The results are shown in Fig. 7.

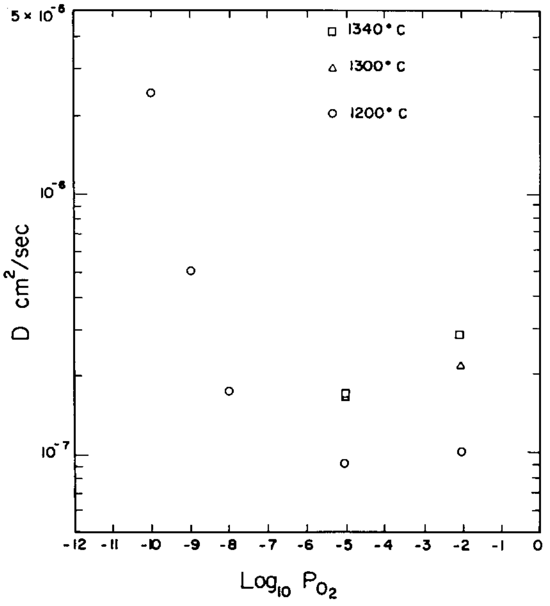

FIG. 6. Chemical diffusion coefficients from reduction of magnesiowüstite as a function of P_{O_2} at 1200, 1300, and 1340°C respectively. P_{O_2} was established with CO/CO mixtures or H_2/H_2O mixtures with similar results at low P_{O_2} atm.

The reduction reactions at $P_{O_2} = 10^{-11}$ and 10^{-10} atm were much faster than for the solid sintered pellet; the new equilibrium was achieved within 1 to 2 min after introduction of the new atmosphere, respectively. This may be compared to the 50–120 min required by the sintered sample. The rates of oxidation were always greater than that of the rates of reduction except at $P_{O_2} = 10^{-11}$ atm which may be too fast to obtain reliable data. This is in contrast to the sintered sample where oxidation was slower than reduction and much slower than for the 35-μm sample.

The reduction rate was slowed down considerably at $P_{O_2} = 9.6 \times 10^{-6}$ atm. The sample reached its new equilibrium within 25 min after being equilibrated in the new reducing atmosphere, but the rate of oxidation was still as fast as the oxidation from lower oxygen partial pressures.

A series reaction such as a gas-surface reaction followed by diffusion in the solid cannot explain the results at low P_{O_2}. In a series reaction the slow step determines the rate. At low P_{O_2} the vacancy concentration is small and diffusion is slow. In order to explain the results it appears that a parallel path to that of diffusion is operative. From studies of micrographs and coloration at the grain boundaries, a grain boundary diffusion model is proposed.

Examination of the microstructure of a water-quenched sample which was reduced from air to $P_{O_2} = 10^{-10}$ atm for 5 min revealed that a green color appears at the external surface and the grain boundaries of the magnesiowüstite. This indicated the formation of ferrous ions at these regions. In the meantime, cation vacancies were also eliminated, according to Eq. (1). The cations, that is both iron and magnesium ions, diffuse toward the center of the grain by cation-vacancy exchanges. In this case the diffusion distance of the cations was only half of a single grain depth instead of the half thickness of the pellet. Hence, the time required to reach the new equilibrium was short. The fast rate of weight loss in this P_{O_2} region is predicted by this proposed mechanism.

In the reduction of a magnesiowüstite slab at very low P_{O_2} (below 10^{-10} atm and at 1200°C), the driving force is the chemical potential difference of oxygen between the solid solution and reducing gas

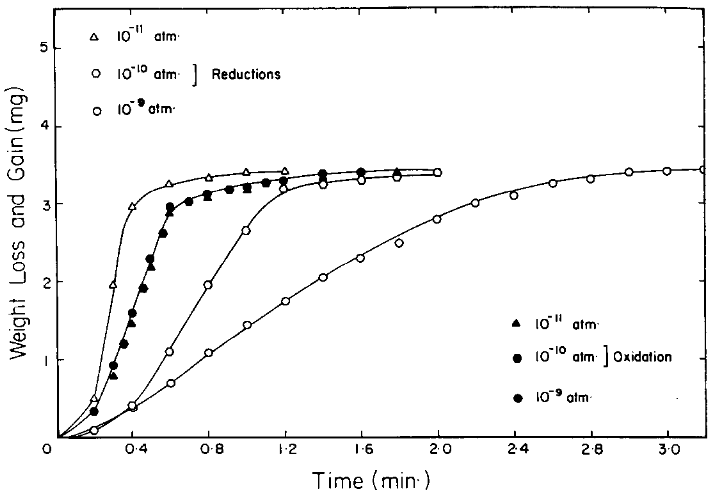

FIG. 7. Reduction and oxidation kinetics of magnesiowüstite particles of about 35 μm diam. at 1200°C.

phase. At these high gradients, the oxygen in the solid solution may escape along the grain boundaries and from the surface of samples according to Eq. (1). In the low P_{O_2} region (10^{-10}–10^{-7} atm and at 1200°C) at the initial stage of the reduction, the reactions can best be interpreted by the desorption of oxygen along the grain boundaries and from the solid solution surface followed by a solid state diffusion process via the exchange of cations and cation vacancies. The overall rate was dependent upon the oxygen partial pressure.

From the kinetics of granular magnesiowüstite, we noted that the rate of oxidation was always greater than the reduction, but the pseudodiffusion coefficients obtained from the oxidation kinetics of large pellets were an order of magnitude smaller than those obtained from the reduction kinetics of the same pellets. This provides us with evidence that at the initial stage of the oxidation, the fast migration paths for oxygen (the grain boundaries) are blocked by the addition of oxygen. The further oxidation of magnesiowüstite required the cations to diffuse through the bulk. The change of reaction mechanism was indicated by the change of curvature of the weight gain rate curve during the initial stage of the oxidation reaction (see Fig. 5).

The experimental results at the higher temperatures (>1250°C) for reduction and oxidation could not be described by parabolic equations. This is indicative of the greater overlap in the surface, grain boundary and diffusion reactions.

Since the chemical diffusion coefficient of iron in magnesiowüstite is a function of cation vacancy concentration and appears to increase linearly with increasing cation vacancies, it can be expressed as follows:

$$\tilde{D} \simeq N_v D_v = N_v D_o \mathrm{e} - \frac{\Delta H^+}{RT}, \tag{4}$$

where

N_v = cation vacancy concentration in fraction of the total cation sites,

D_v = diffusivity of the cation vacancy in magnesiowüstite solid solution,

ΔH^+ = activation energy for migration of the vacancy.

The vacancy concentration equilibrated with the reducing (or oxidation) atmosphere is used in Eq. (4). The activation energy, ΔH^+, of the weight gain or loss is obtained from the $\log D/N_v$ versus $1/T$ plot. For the reduction at $P_{O_2} = 0.0164$ and 9.6×10^{-6} atm and oxidation at $P_{O_2} = 0.0164$ atm, the numerical value 45 kcal/mol was determined to be the activation energy of the diffusion of iron in magnesiowüstite solid solutions. This value is in good agreement with Rigby's 47.5 kcal/mol.

Figure 9 shows the diffusivities of various impurity ions in MgO and iron in Fe_xO. The results from present work are also plotted for a comparison. It appears that the chemical diffusivities of iron in polycrystalline magnesiowüstite are higher than those obtained from interdiffusion studies.

The chemical diffusivity of ion in wüstite investigated by Hembree and Wagner (*14*) and Levin and Wagner (*12*) by using tracer and thermogravimetric methods, respectively, yielded different results. In tracer studies, the chemical diffusivity increased

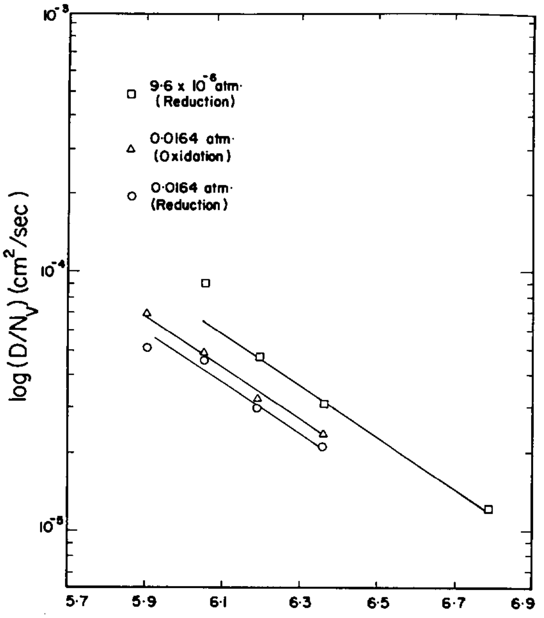

FIG. 8. Logarithm (D/N_v) versus reciprocal temperature by reduction and oxidation of magnesiowüstite pellets. The lines drawn through the points represent 45 kcal/mol activation energy.

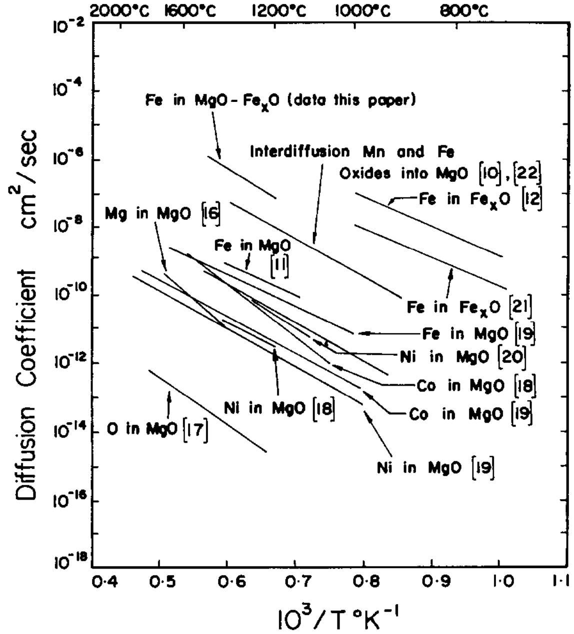

FIG. 9. Diffusivities of ions in MgO and Fe$_x$O. Showing the data described in this paper in relation to other publications.

linearly with iron vacancies but decreased with increasing iron vacancies in thermogravimetric studies. Recently, Campbell (*23*) measured interdiffusion in Fe$_x$O by thermogravimetric measurement and he found results similar to Hembree. Both interdiffusions studies in Mn$_x$O–MgO and Fe$_x$O–MgO systems revealed that the diffusivities increased with increasing cation vacancy concentration.

From Hembree's work and the results in this presentation, we may suspect that the migration of oxygen along the grain boundary at the initial stage of the reduction may also occur in the system of reduction of wüstite. This eventually will result in decreasing the diffusivity of iron in wüstite with increasing cation vacancy. The observed diffusivity may only be the pseudodiffusivity. The tracer work and the results here have indicated that the diffusivity of iron in wüstite and magnesiowüstite are indeed increasing with increasing cation vacancy concentration.

Conclusion

Thermogravimetrical studies of the reduction of polycrystalline magnesiowüstite solid solutions revealed that the reduction kinetics in high oxygen partial pressure atmospheres (0.18–9.6 × 10^{-6}) and 1200–1420°C are cation (Fe) diffusion controlled. The chemical diffusion coefficient of iron in magnesiowüstite was found to increase with increasing cation vacancies. The activation energy was 45 kcal/mol for the diffusion process of iron in magnesiowüstite.

The pseudochemical diffusion coefficient of iron in magnesiowüstite evaluated from the reduction kinetics in 10^{-10}–10^{-7} atm oxygen partial pressure region decreased as the cation vacancy concentration increased. The reduction kinetics could be interpreted best by assuming an initial desorption of oxygen on the solid surface and migration of oxygen through the grain boundaries and followed by associated solid state diffusion process.

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