Decarburization Kinetics of Fe–C–S Droplets with H₂O

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Decarburization of liquid Fe–C–S droplets with H₂O vapour was investigated using the electromagnetic levitation technique. The results indicated that the decarburization of liquid iron droplets by H₂O vapour can be adequately described by the mixed control of the gas phase mass transport and the dissociative chemisorption of H₂O at the melt surface. The Steinberger–Treybal correlation equation was found to correctly represent the gas phase mass transfer in the present system geometry and experimental conditions. The rate of decarburization decreased significantly with increase in sulphur content in the melt, and this effect was quantitatively represented by the mixed control model. There exists a residual rate of decarburization at high sulphur contents in the melt. The extent of the residual rate observed can be interpreted as implying that, even at the melt surface of apparent saturation with sulphur, 8–9% of the surface sites are still available for H₂O molecules to react with carbon. The activation energy of dissociative chemisorption of H₂O was 95 kJ mol^{−1}.

KEY WORDS: decarburization; water vapour; mass transfer coefficient; levitation; kinetics; reaction rate.

1. Introduction

Achievement of high efficiencies of post combustion and heat transfer is of importance in the development of smelting reduction ironmaking processes.^{1–6)} There are two strategies which are commonly employed; namely, use of a deep foaming slag as energy transfer medium^{1–3)} and, use of metal and slag droplets generated by high intensity of turbulence of the smelting bath.^{4–6)} In the latter case, a large number of droplets pass through the post-combusted gases at the top space of the bath, and hence heat is transferred to the droplets. The reaction characteristics of liquid droplets in the post combustion gases has a significant influence on the efficiency of smelting reduction processes. Of particular interest is the reactions of liquid Fe–C–S droplets with H₂O in the gas phase, as smelting reduction processes may give off a significant amount of water vapour to the top space.⁷⁾

Decarburization with water vapour has not been extensively investigated. Consequently information on the chemical kinetic characteristics of the reaction is lacking. Early work^{8,9)} was conducted under conditions where decarburization was predominantly controlled by the gas phase mass transport. Fruehan *et al.*¹⁰⁾ investigated the decarburization reaction with carbon saturated iron melts using a crucible technique. They found that even with gas velocities as high as 13 m s^{−1}, decarburization with water vapour encountered upto 10% resistance from the mass transfer in the gas phase. The dissociative chemisorption of the H₂O molecule on the melt surface

was deemed to be the slowest for the surface decarburization reaction.

In the present work, it was attempted to determine reaction rates and the rate limiting mechanism for the decarburization of levitating Fe–C–S melt droplets with water vapour. The effects of the partial pressure of H₂O, gas flowrate, melt compositions and temperature on the rate of decarburization were examined.

2. Experimental

The decarburization experiments were carried out by levitating liquid Fe–C–S droplets in a flowing gas stream in order to simulate metal drops flying in the top space of a smelting bath. Samples of iron alloys weighing 0.8 g were prepared from spectrographically pure reagents. A sample for reaction was placed in the levitation position within the coil (**Fig. 1**). The reaction vessel was flushed with argon gas for an appropriate period. The coil was then energised at the lowest power level which was then slowly raised to the pre-determined level so as to melt and support the sample. The levitating liquid drop was allowed to stabilize in its position and the temperature was brought to 1723 K by adjusting the power to the coil. The fourway stopcock and the generator timer were simultaneously switched to introduce pre-mixed and metered reaction gas for a prescribed duration. Control of the melt temperature was maintained during the reaction by manipulating the power to the coil. On completion of the reaction the generator shut down,

Fig. 1. Schematic diagram of experimental apparatus.

dropping the sample into a helium and water-cooled quench mould. The sample was removed from the mould and suitably stored. The quenched samples were then analyzed using combustion/IR spectrometry (CS444 Leco Analyser) and the rates of decarburization were obtained from the raw experimental data. In order to produce and maintain steam in its vapour form, a steam generator was used. Stoichiometric amounts of hydrogen and oxygen were metered into the burner contained in a glass reaction vessel. The gas mixture was ignited at the mouth of the burner by a heated platinum filament. The steam carrying conduits from the generator upto the delivery lance of the levitation reactor were kept heated using a resistance heating tape. The temperature of the gas mixture delivered to the levitation reactor was kept at 450 K.

3. Results and Discussion

Decarburization rates obtained for all experimental conditions employed in this investigation are given in Table 1. The change in carbon concentration with time at different partial pressures of H_2O and flowrates is shown in Fig. 2. It clearly indicates that the rate of decarburization of the melt is independent of the bulk carbon concentration until the melt composition reaches the liquidus at 1.24 mass% carbon at 1723 K.¹²⁾ This linear relationship was also observed for all other experimental conditions, *i.e.*, different sulphur concentrations and temperatures employed in this study. For the present conditions, therefore, it can be concluded that the liquid phase transport of carbon has no effect on the rate of decarburization with H_2O vapour. This is in agreement with literature.¹⁰⁾ Similar observations have been reported for the decarburization with other oxidants including CO_2 and O_2 .¹³⁻¹⁸⁾ Once the liquidus was reached by decrease in carbon to 1.24 mass%, levitation conditions were unstable and therefore the reaction was discontinued.

Table 1. Experimental results on decarburization using H_2O vapour.

Gas compositions (%)		Gas flowrate ($\text{m}^3\text{min}^{-1}$)	T (K)	Sulphur (mass %)	-d%C/dt (mass% s ⁻¹)
H_2O	N_2				
5	95	0.0147	1723	<0.0005	0.0231
10	90	0.0147	1723	<0.0005	0.0495
15	85	0.0147	1723	<0.0005	0.0718
20	80	0.0147	1723	<0.0005	0.1000
10	90	0.0073	1723	<0.0005	0.0377
10	90	0.0103	1723	<0.0005	0.0417
10	90	0.0175	1723	<0.0005	0.0501
10	90	0.0222	1723	<0.0005	0.0569
10	90	0.0147	1723	0.0025	0.0470
10	90	0.0147	1723	0.0110	0.0401
10	90	0.0147	1723	0.0550	0.0344
10	90	0.0147	1723	0.1010	0.0285
10	90	0.0147	1723	0.2700	0.0204
10	90	0.0147	1693	<0.0005	0.0492
10	90	0.0147	1773	<0.0005	0.0521
10	90	0.0147	1823	<0.0005	0.0536

Fig. 2. Change of carbon content with reaction time at different H_2O partial pressures.

3.1. Gas Phase Transport

Experiments were conducted in environments containing H_2O in the range of 5 to 20% with N_2 as diluent gas to investigate the effect of H_2O partial pressure. The gas flowrate was maintained at $0.0147 \text{ m}^3 \text{ min}^{-1}$ and the sulphur content in the melt was less than 5 ppm. The results are given in Fig. 3 which shows that the rate of decarburization increases linearly with the partial pressure of H_2O . The overall process of decarburization by H_2O may be represented by the following reaction:

This reaction may be divided into a number of elementary steps:

1) Gas phase transport of H_2O

Fig. 3. Effect of H_2O partial pressure on the rate of decarburization.

2) Dissociative chemisorption of H_2O at the metal surface

3) Decarburization reaction

4) Desorption of CO^*

5) Transport to the bulk gas phase

where v is a vacant site on the metal surface available for H_2O adsorption and the superscript $*$ represents the adsorbed state.

If the gas phase mass transport of H_2O is the rate limiting step, Eq. (2) results in the following rate equation:

$$-\frac{d(\%C)}{dt} = \frac{1}{\rho_m V} \frac{200A}{RT_f} \frac{k_g}{1 + P_{H_2O}^i} \ln \left(\frac{1 + P_{H_2O}^b}{1 + P_{H_2O}^i} \right) \quad \text{mass\% s}^{-1} \quad \text{.....(8)}$$

where A is the interfacial area, ρ_m is the molar density of the sample, V is the volume of the sample, k_g is the gas phase mass transfer coefficient, T_f is the film temperature, and the superscripts b and i represent bulk and interfacial states, respectively.

Ignoring the partial pressure of H_2O at the interface, Eq. (8) is reduced to

$$-\frac{d(\%C)}{dt} = \frac{1}{\rho_m V} \frac{200A}{RT_f} \frac{k_g}{1 + P_{H_2O}^b} \ln(1 + P_{H_2O}^b) \quad \text{mass\% s}^{-1} \quad \text{.....(9)}$$

This equation predicts a linear relationship of the rate of decarburization with $\ln(1 + P_{H_2O}^b)$. **Figure 4** proves that this is the case. In order to check the validity of the above, the theoretical prediction of decarburization rates under assumption that the rate is solely controlled by the gas phase mass transfer is also superimposed in the

Fig. 4. Effect of H_2O partial pressure on the rate of decarburization. Predictions by the gas phase mass transport control are included.

figure. For this the mass transfer coefficient in the gas phase, k_g , can be calculated using Steinberger and Treybal's correlation equation¹⁹⁾:

$$Sh = 2 + 0.569(Gr' Sc)^{0.25} + 0.347 Re^{0.62} Sc^{0.31} \quad \text{....(10)}$$

In order to use the above equation, it is necessary to determine the physical properties of the gas mixture in the boundary layer. The determination of gas properties in levitation conditions is made difficult due to temperature and concentration gradients that are developed in the reaction system. For this investigation, the gas properties were determined at the film temperature T_f using relationships documented by Bird *et al.*²²⁾ and Perry *et al.*²³⁾ In the case of decarburization controlled by mass transport in the gas phase, the interfacial reaction is considered to be at equilibrium, and hence the gas phase at the interface will mainly consist of N_2 , H_2 and CO . On the other hand, the bulk gas comprises N_2 and H_2O , and thus the gas compositions in the boundary layer should change along the radial direction. However, the change in the gas composition within the boundary layer is not large, since more than 80 % in the gas is nitrogen for all the gas mixtures employed in the present study. Hence, the change in the physical properties with the change in gas composition in the boundary layer should be small. Hence a binary gas approximation consisting of nitrogen and steam is used to calculate the respective gas properties. This approximation has been justified by comparison of k_g 's calculated using Eq. (10) with two different gas compositions, namely, the bulk gas composition and the arithmetic mean of the bulk and interfacial compositions. The two values agree with each other within 3 %. For example, the value of k_g was found to be 0.34 m s^{-1} for the experimental conditions shown in Fig. 4 when the bulk gas composition was used in the calculation. If the arithmetic mean composition of the bulk and interface is used, this value is calculated to be 0.35 m s^{-1} . Therefore, use of the bulk gas composition for calculation of the gas properties does not introduce unacceptable errors, in particular, considering the inherent uncertainties associated with Eq. (10) itself. The

Table 2. Calculated gas properties at film temperature for experimental conditions.

Properties Gas compositions	Viscosity (μ)	Diffusivity (D_{AB})	Thermal conductivity (κ)	Heat capacity (C_p)	Density (ρ)
	$\times 10^3$ P	$\times 10^4$ m ² s ⁻¹	JK ⁻¹ s ⁻¹ m ⁻¹	kJkg ⁻¹ K ⁻¹	kgm ⁻³
5%H ₂ O-95% N ₂	0.42	2.23	0.067	1.23	0.31
10%H ₂ O-90% N ₂	0.41	2.23	0.068	1.29	0.31
15%H ₂ O-85% N ₂	0.41	2.23	0.069	1.35	0.30
20%H ₂ O-80% N ₂	0.40	2.23	0.069	1.41	0.30

gas properties computed using the bulk gas compositions are listed in **Table 2** for the various gas mixtures used in this work.

It is noted in Fig. 4 that although the measured values of the rate show a linear relationship with $\ln(1 + P_{H_2O}^b)$, they are consistently lower than the values predicted under the assumption of gas phase mass transfer control. It is also noted in Fig. 3 that the same measured values gave rise to an equally valid linear relationship with $P_{H_2O}^b$. This is because $P_{H_2O}^b \approx \ln(1 + P_{H_2O}^b)$ at low $P_{H_2O}^b$. Therefore, these apparent first order relationships are not sufficient, on their own, to distinguish between rates limited by gas phase mass transport and by interfacial chemical kinetics.

In order to test for the effect of gas phase mass transport, the rates of decarburization were obtained at different gas flowrates ranging from 0.0075 to 0.0225 m³ min⁻¹. This range represents an exit gas velocity from 1.10 to 3.32 m s⁻¹. The partial pressure of steam was maintained at 0.1 atm with the diluent gas of nitrogen and the sulphur content of the melt was kept below 5 ppm. As shown in **Fig. 5**, the decarburization rate increases with increasing gas flowrate. Since the increase in the gas flowrate increases the gas phase mass transfer coefficient, this observation is characteristic of a process whose rate is affected by the gas phase mass transfer. It is seen in Eq. (10) that the gas flowrate influences the third term in the right hand side of the equation, which reflects the effect of the forced convection. Included in Fig. 5 are the rates of decarburization predicted using Eq. (10) under assumption that the rate is controlled solely by the gas phase transport. It is seen from the figure that the predicted rate is consistently higher than the measured one over the range of flowrate examined, but gradually approaches the measured one, as the flowrate decreases.

Earlier work¹⁰⁾ has shown that the transport of CO from the reaction interface to the bulk gas has no effect on the rate of decarburization even at the CO partial pressure of 0.9 atm. This was also verified in the concurrent work by the authors¹⁸⁾ with CO and CO₂. Transport properties of H₂ are much larger than other gases,²⁰⁾ and hence the transport of H₂ in the gas phase should not exert resistance to the decarburization.

In summary, it can be concluded from observations described above that the gas phase mass transport of H₂O vapour plays a main role in determining the rate

Fig. 5. Effect of gas flowrate on the rate of decarburization with H₂O. Predictions by the gas phase mass transport control are included.

of decarburization under the present experimental conditions.

3.2. Interfacial Reactions

Earlier work¹⁰⁾ have shown that, of three interfacial reactions represented by Eqs. (3) to (5), the latter two reactions are not considered to be rate controlling. This view is further supported by the report¹⁴⁾ on decarburization with CO₂ in that these two reactions were found not rate limiting for the interfacial reaction. From Eq. (3), therefore, the rate of decarburization can be represented by the following equation:

$$-\frac{d(\%C)}{dt} = \frac{1200A}{\rho_m V} k_c C_v P_{H_2O}^i \text{ mass\% s}^{-1} \dots (11)$$

where k_c is the rate constant of the forward reaction of Eq. (3), and C_v is the fractional surface site which is available for H₂O adsorption. If the decarburization is solely controlled by the dissociative chemisorption of H₂O at the melt surface, $P_{H_2O}^i$ in Eq. (11) would be almost the same as the bulk pressure of H₂O, $P_{H_2O}^b$. However, it was discussed earlier that the resistance from the gas phase transport is not negligible. In order to describe the decarburization kinetics with H₂O in a proper manner, therefore, it is necessary to consider both the gas phase mass transport and interfacial chemical reaction. Thus,

a mixed control model can be derived by combining Eqs. (8) and (11). Combination of these two equations by eliminating $P_{\text{H}_2\text{O}}^i$ yields

$$-\frac{d(\%C)}{dt} = \frac{1200A}{\rho_m V} \left(\frac{k_g^\circ k_c C_v}{k_g^\circ + k_c C_v} \right) \ln(1 + P_{\text{H}_2\text{O}}^b) \quad \text{mass\% s}^{-1} \quad \text{..... (12)}$$

where $k_g^\circ = k_g/(RT_f)$.

Equation (12) thus represents the rate of decarburization under the mixed control by both the gas phase mass transfer and the dissociative chemisorption of H_2O . This equation predicts a linear relationship between the rate of decarburization and $\ln(1 + P_{\text{H}_2\text{O}}^b)$ for a given melt composition. Since sulphur is surface active in liquid iron, its presence in the melt will significantly reduce the value of C_v in the above equation. If sulphur is the only element which blocks sites for H_2O adsorption, C_v can be represented by Eq. (13):

$$C_v = 1 - \theta_s \quad \text{..... (13)}$$

where θ_s is the fractional surface sites occupied by sulphur.

There may also exist some surface sites which cannot be blocked by sulphur: the reason for this being either stirring effect of the melt, the penetration of H_2O molecules through the chemisorbed sulphur layer when arrived at a particular orientation, residual disorder, misfit in the chemisorbed surface layer or hydrodynamic effects of the melt. If we accept one of the above possibilities and adopt the Langmuir isotherm for sulphur adsorption,

$$K_s = \frac{\theta_s}{(1 - \theta_s - \theta_U)a_s} \quad \text{..... (14)}$$

where K_s is the adsorption coefficient of sulphur, θ_U is the fractional surface sites which are not available for sulphur adsorption, and a_s is the sulphur activity in the bulk metal.

Combination of Eqs. (13) and (14) yields

$$C_v = \frac{1 + \theta_U K_s a_s}{1 + K_s a_s} \quad \text{..... (15)}$$

Effect of sulphur on decarburization can thus be adequately represented by Eq. (12) together with Eq. (15). **Figure 6** shows the experimental results of decarburization with H_2O vapour at different sulphur contents in the melt. It is clearly seen that the rate decreases with increase in the sulphur content. Superimposed in Fig. 6 are the rates of decarburization calculated by curve fitting using Eq. (12). The value of k_g° used in the calculation is $4 \text{ mol m}^{-2} \text{ s}^{-1}$ which was obtained from the earlier calculation using the Steinberger–Treybal equation, Eq. (10). The value of K_s was determined to be 200 by a separate study for CO_2 decarburization,²¹⁾ which employed the same experimental setup as the present study. However, Belton⁷⁾ has recommended 450 for K_s at 1450°C . The reason for this discrepancy is not immediately clear. Nevertheless, the values of k_c and θ_U were determined by regression for the best fitting of Eq. (12) to the present results. These were found to be

Fig. 6. Effect of sulphur on the rate of decarburization with H_2O . Predictions by the mixed control model are also included.

$20 \text{ mol m}^{-2} \text{ s}^{-1}$ and 0.09, respectively, with $K_s = 200$, and $25 \text{ mol m}^{-2} \text{ s}^{-1}$ and 0.08 with $K_s = 450$. The reliability of these calculated values is dependent on the accuracy of the values of k_g° and K_s chosen. As seen above, however, k_c and θ_U have been found not to sensitively vary with K_s . Sasaki *et al.*¹¹⁾ has reported the value of $35 \text{ mol m}^{-2} \text{ s}^{-1}$ ($\pm 35\%$) for the rate constant (k_c) of the dissociative chemisorption of H_2O at 1723 K . Fruehan *et al.*¹⁰⁾ has reported a higher value of $55 \text{ mol m}^{-2} \text{ s}^{-1}$. The reason for the discrepancy between the investigators is not immediately clear. It may be the difference in the system geometry. Incoming oxidants are not likely to be uniformly distributed over the entire interfacial area. For the levitation geometry like the one employed in the present work there may exist a significant variation of the gas dynamics around the levitating drop. For the crucible method employed by the other investigators,^{10,11)} the distribution of oxidants may vary to a significant extent across the radial direction in the crucible. Therefore, the use of the geometric area for the interfacial reaction area in the calculation of the rate constant may result in a value which is geometry-specific.

The value of 0.08–0.09 for θ_U obtained in the above can be interpreted as implying that, even at the melt surface of apparent saturation with sulphur, 8–9% of the surface sites are still available for H_2O molecules to react with carbon. This gives rise to a residual rate of decarburization at high sulfur contents in the melt. In the concurrent work by the authors²¹⁾ with CO_2 , it was found that θ_U is 0.014. Sain and Belton¹⁴⁾ also reported the value of 0.014 from the results of CO_2 decarburization by crucible method. But Lee and Rao¹⁷⁾ reported the values of 0.085 from CO_2 decarburization by levitation technique. Therefore the residual rate of decarburization appears to be influenced by a number of factors including the system geometry, oxidising species, and the hydrodynamics of the melt.

In summary, decarburization of liquid iron droplets by H_2O vapour can be adequately described by the mixed control of the gas phase mass transport and dissociative

Fig. 7. Effect of temperature on the rate of decarburization with H₂O.

Fig. 8. Effect of temperature on the reaction constant of dissociative chemisorption of H₂O at the iron melt surface.

chemisorption of H₂O on the melt surface. The relative resistances of the gas phase mass transport and the interfacial reaction to the overall decarburization can be calculated from the values of k_g° and k_c obtained above, and these are 85 and 15 %, respectively. Fruehan *et al.*^[10] have reported that even with the gas velocity of 13 m s⁻¹ they still encountered about 10 % resistance from the gas phase mass transfer.

3.3. Activation Energies

In order to elucidate the effect of temperature on the decarburization with H₂O vapour, experiments were carried out at a number of different temperatures and the results are shown in Fig. 7. It is clear that there is an increase in the rate of decarburization with increasing temperature. Since the gas phase mass transfer coefficients at different temperatures can be obtained using the Steinberger–Treybal equation, Eq. (10), it is possible to calculate the reaction rate constants at the corresponding temperatures using the following relationship:

$$\frac{1}{k_{app}} = \frac{1}{k_g^\circ} + \frac{1}{k_c} \quad \dots\dots\dots (16)$$

The results are given in Fig. 8 together with those reported by other investigators. The activation energy of dissociative chemisorption of H₂O found from the present study is 95 kJ mol⁻¹. The activation energies of 58 and 92 kJ mol⁻¹ are obtained from the works of Sasaki *et al.*^[11] and of Fruehan *et al.*^[10] respectively. These values are in reasonable agreement with each other.

4. Conclusions

Decarburization of liquid Fe–C–S drops was investigated using H₂O vapour by the electromagnetic levitation technique. Findings from this study are summarised in the following:

- (1) Decarburization of liquid iron droplets by H₂O vapour can be adequately described by the mixed control of the gas phase mass transport and the dissociative chemisorption of H₂O at the melt surface.
- (2) The Steinberger–Treybal correlation equation appears to represent the gas phase mass transfer in the present system geometry and experimental conditions.
- (3) The rate of decarburization decreases significantly with increase in sulphur content in the melt, and this effect is quantitatively represented by the mixed control model.
- (4) There exists a residual rate of decarburization was observed at high sulphur contents in the melt. The extent of the residual rate observed can be interpreted as implying that, even at the melt surface of apparent saturation with sulphur, 9 % of the surface sites are still available for H₂O molecules to react with carbon.
- (5) The activation energy of dissociative chemisorption of H₂O is 95 kJ mol⁻¹.

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Nomenclature

- A : interfacial area (m²)
- ρ_m : molar density of metal (mol m⁻³)
- V : volume of the sample (m³)
- k_g : gas mass transfer coefficient (m s⁻¹)
- v : vacant site
- k_c : forward rate constant of dissociative chemisorption of CO₂ (mol m⁻² s⁻¹)
- C_v : fractional surface site available for CO₂ adsorption
- T_a : ambient temperature (K)
- T_s : melt temperature (K)
- T_f : film temperature ($= (T_a + T_s)/2$) (K)
- T_c : critical temperature (K)
- P_c : critical pressure
- k_g° : gas mass transfer coefficient ($= k_g/RT_f$) (mol m⁻² s⁻¹)
- Sh: Sherwood number ($= k_g d/D$)
- Gr': Mean Grashof number ($= Gr_m + (Sc/Pr)^{0.5} Gr_h$)

- Sc: Schmidt number ($=\mu_f/\rho_f D$)
 Re: Reynolds number ($=\rho_f d v/\mu_f$)
 Gr_m: Grashof number for mass transfer
 ($=\rho_f g d^3(\rho_i - \rho_b)/\mu_f^2$)
 Gr_h: Grashof number for heat transfer
 ($=\rho_f^2 g d^3(\rho_i - \rho_b)/\mu_f^2 T_f$)
 Pr: Prandtl number ($=\mu_f C_p/\kappa$)
 d: diameter of sample (m)
 D: interdiffusivity in the gas mixture ($\text{m}^2 \text{s}^{-1}$)
 μ : viscosity of gas ($\text{kg m}^{-1} \text{s}^{-1}$)
 ρ : density of gas (kg m^{-3})
 v: velocity of gas (m s^{-1})
 C_p: heat capacity of gas ($\text{J kg}^{-1} \text{K}^{-1}$)
 κ : thermal conductivity of gas ($\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$)
 g: acceleration due to gravity (m s^{-2})
 θ_S : fractional surface sites occupied by sulphur
 θ_U : fractional surface sites not available for sulphur adsorption
 K_S: adsorption coefficient of sulphur
 a_S: activity of sulphur
 M: molecular weight
 Superscripts
 b: bulk property
 i: interfacial property
 *: adsorbed state
 Subscript
 f: film temperature property

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