

Communications

Factors Influencing Dissolution of Carbonaceous Materials in Liquid Iron

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Carbon dissolution into liquid iron was investigated by a kinetic model assuming the rate is limited by interfacial carbon dissociation and mass transfer in the liquid iron. The rate influencing factors and the inter-relations among them were discussed with the aid of the kinetic model.

Carbon dissolution into liquid iron has been intensively studied with various carbonaceous materials due to its importance in future blast furnace ironmaking and alternative iron smelting processes. The rate of this reaction was conventionally considered to be limited by the mass transfer in liquid iron.^[1-6] In the recent studies with various carbonaceous materials, the interfacial dissociation reaction was suggested to be slow for the materials with complex structure, such as coal.^[7,8,9] This requires a kinetic treatment of observed rates that includes interfacial reaction and mass transfer. In this study, a kinetic model is presented and the rate influencing factors are discussed with the aid of the kinetic model.

When a solid carbon material contacts with liquid iron, the dissolution of carbon occurs through two elementary steps: the first step is the dissociation of carbon atoms from solid structure into the liquid at the solid-liquid interface, as shown by Eq. [1], and its rate is written as Eq. [2] for a reversible reaction:



$$r_r = Ak_r \left(a_{\text{solid}} - \frac{a_C^*}{K_r} \right) \quad [2]$$

The second step is the mass transfer of carbon from the interface into liquid bulk, as shown by Eq. [3], and its rate is given by Eq. [4] for a diffusion process:



$$r_m = \frac{Ak_m \rho_m}{100} ([C]^* - [C]) \quad [4]$$

Since two steps occur in series, the dissolution rate is

$$r_d = r_r = r_m \quad [5]$$

Equating Eq. [2] with Eq. [4] and using the activity relation at the interface, $a_C^* = f_C^* [C]^*$, the carbon content at the interface can be obtained as

$$[C]^* = \frac{k_r a_{\text{solid}} + \frac{k_m \rho_m}{100} [C]}{\frac{k_r f_C^*}{K_r} + \frac{k_m \rho_m}{100}} \quad [6]$$

Replacing $[C]^*$ in Eq. [4] with Eq. [6], the carbon dissolution rate is given by

$$r_d = Ak_t \left(a_{\text{solid}} - \frac{f_C^* [C]}{K_r} \right) \quad [7]$$

where

$$\frac{1}{k_t} = \frac{1}{k_r} + \frac{100 f_C^*}{k_m \rho_m K_r} \quad [8]$$

Equation [7] involves interfacial reaction and mass transfer. The driving force is $a_{\text{solid}} - f_C^* [C]/K_r$. There is no integration form of Eq. [7] because k_t and f_C^* vary with $[C]^*$ and the latter varies with $[C]$.

When the carbon dissolution is limited by mass transfer, *i.e.*, $100 f_C^* / k_m \rho_m K_r \gg 1/k_r$, the equilibrium of Reaction [1] will be achieved at the interface. It gives $[C]^* = [C]^{\text{sat}}$, $f_C^* = f_C^{\text{sat}}$, and $a_C^* = a_C^{\text{sat}}$. The rate equation becomes

$$r_d = \frac{Ak_m \rho_m}{100} ([C]^{\text{sat}} - [C]) \quad [9]$$

The driving force is $[C]^{\text{sat}} - [C]$. The rate is dictated by k_m and $[C]^{\text{sat}}$: the former varies with temperature, liquid composition, and liquid-phase agitation, and the latter with temperature, liquid composition, and solid structure. Equation [9], or its integrated form as given in Eq. [10], is frequently used when liquid-phase mass transfer was the solely limiting step.

$$\ln \frac{([C]^{\text{sat}} - [C])}{([C]^{\text{sat}} - [C]_0)} = \frac{Ak_m}{V_m} t \quad [10]$$

When the carbon dissolution is limited by the dissociation reaction, *i.e.*, $1/k_r \gg 100 f_C^* / k_m \rho_m K_r$, interfacial values are equal to their bulk counterparts, *i.e.*, $[C]^* = [C]$, $f_C^* = f_C$, and $a_C^* = a_C$, and the rate becomes

$$r_d = Ak_r \left(a_{\text{solid}} - \frac{a_C}{K_r} \right) \quad [11]$$

The driving force is $a_{\text{solid}} - a_C/K_r$. Since $a_{\text{solid}} = 1$, the rate is dictated by k_r , a_C , and K_r . The value of k_r varies with temperature, structure of solid, and interfacial active elements. The value of a_C varies with temperature and liquid composition, and K_r varies with temperature and solid structure.

Alternatively, using carbon contents in equilibrium with solid and an instantaneous f_C from the equilibrium relation of Reaction [1], $[C]_{\text{eq}} = K_r a_{\text{solid}} f_C$, the rate equation becomes

$$r_d = Ak_r' ([C]_{\text{eq}} - [C]) \quad [12]$$

where

$$k_r' = \frac{f_C}{K_r} k_r \quad [13]$$

The driving force is then $[C]_{\text{eq}} - [C]$. Equation [12] has a similar form as Eq. [9] for mass transfer limiting. However,

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k'_r and $[C]_{eq}$ in Eq. [12] vary with f_C ; this forbids Eq. [12] to be integrated into similar form as Eq. [10] because f_C varies with carbon content.

For all of the cases discussed previously, the dissolution rate is influenced by the contact area A . The dissolution rates are sensitive to k_m when mass transfer is involved (Eqs. [7] and [9]) and to k_r and K_r when interfacial reaction is involved (Eqs. [7] and [11]). The term $[C]^{sat}$ directly involves driving force when mass transfer is the solely limiting step.

The factors that influence the carbon dissolution rate can be investigated by their influence on the kinetic and thermodynamic parameters, A , k_m , k_r , K_r , or $[C]^{sat}$. Temperature will not directly affect A , but it may, through affecting wettability between solid carbon and liquid, viscosity, and fusion of ash, change A . Temperature has a stronger impact on k_r than on k_m . The values of K_r and $[C]^{sat}$ are dependents of temperature. The structure of carbon solid may affect k_r , and slightly affect K_r and $[C]^{sat}$. This is because k_r describes the dissociation rate of carbon atoms from the solid lattice. The term K_r is related to the free energy change of Reaction [1], which depends on the solid structure. Graphite, various cokes and coals, and diamond are carbon of different structures and have different K_r values at a given temperature. The term $[C]^{sat}$, varying with K_r , is affected by solid structure. Interfacial active elements such as S will occupy the reaction sites to reduce k_r . Alloying elements, such as Si, Mn, and S, will affect f_C and $[C]^{sat}$. Liquid agitation increases k_m but will not affect other rate parameters. When porous or small particles of carbon solid are in contact with the liquid, good wetting of liquid to the solid will allow liquid to penetrate into pores of solid or interstitial space between particles to increase the contact area. Ash in carbonaceous materials would accumulate at the interface and become a physical barrier at the interface during carbon dissolution for materials containing ash, which will reduce contact area available for further carbon dissolution. The "strength" of the physical barrier depends on viscosity, fusion temperature, and wetting characters between ash and iron or solid carbon. Ash components also provide reactant for side reactions. The side reactions will not directly affect the carbon dissolution rate, but they may consume dissolved carbon or change metal composition to influence the rate. The CO generated from reduction reactions of ash components will contribute to the liquid-phase agitation to increase k_m . The strength of the physical barrier may also be affected by side reactions since ash composition and therefore viscosity, fusion temperature, and wetting characters will change as a result of these reactions.

In summary, the driving force, kinetic, and thermodynamic parameters for carbon dissolution limited by mass transfer are different from those by interfacial reaction. In an experimental study of the kinetics of the dissolution process of various carbonaceous materials, efforts should be made to isolate the rate influencing factor of interest to avoid the influence being masked by the variation of other rate influencing factor(s).

SYMBOLS

A	solid-liquid contact area (cm ²)
a_{solid} , a_C , and a_C^*	activities of carbon in solid, in liquid, and at interface, respectively

$C_{(solid)}$	solid carbon
$[C]$, $[C]^*$, $[C]^{sat}$ and $[C]_0$	carbon contents in liquid, at interface, of saturation, and in initial liquid, respectively (mass pct)
f_C , f_C^* , and f_C^{sat}	carbon activity coefficients in liquid, at the interface, and in the liquid saturated with carbon
K_r	equilibrium constant for Reaction [1]
k_r	rate constant of Reaction [1] for rate Eq. [11] (g/s cm ²)
k'_r	rate constant of Reaction [1] for rate Eq. [12] (g/s cm ²)
k_m	mass-transfer coefficient in liquid (cm/s)
k_i	overall rate constant of carbon dissolution (g/s cm ²)
r_r , r_m , and r_d	rates of the dissociation reaction, mass transfer, and dissolution of carbon (g/s)
V_m	volume of liquid iron (cm ³)
ρ_m	density of liquid (g/cm ³)

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Discussion of "The Influence of Chemical Equilibrium on Fluid-Solid Reaction Rates and the Falsification of Activation Energy"*

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In a recent article, Sohn^[1] tried to establish, by way of demonstrating the importance of thermodynamics in kinetic

*H.Y. SOHN: *Metall. Mater. Trans. B*, 2004, vol. 35B, pp. 121-31.
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