

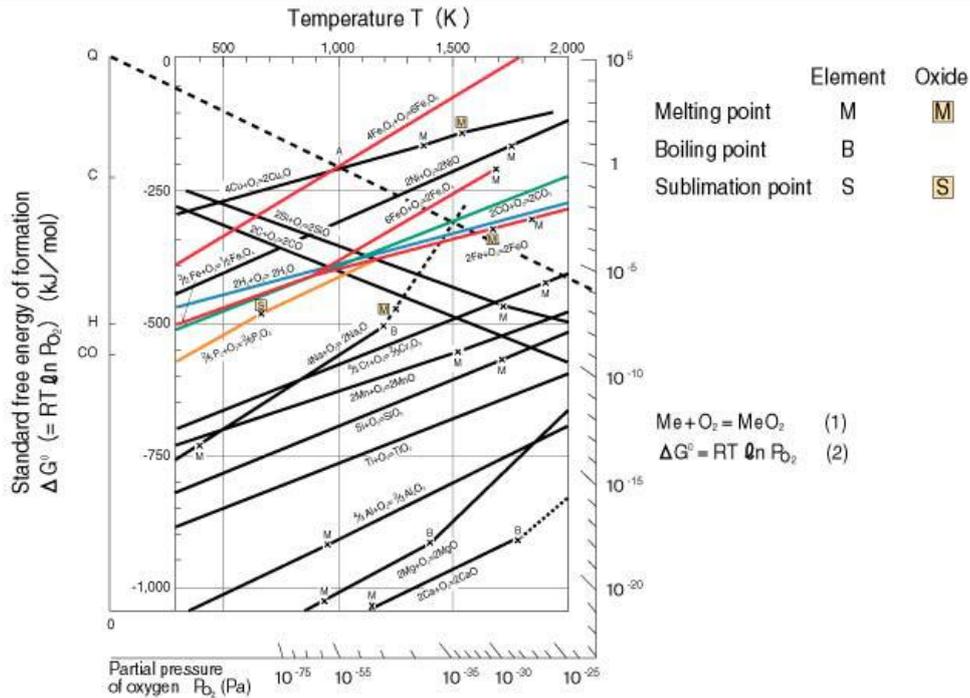
Basic Principles for Smelting and Refining

● Ellingham Diagram

The chemical reactions occurring in metallurgical processes such as the reduction of iron ore and the decarburization of molten iron can be explained in terms of the free energy in thermodynamics. When the free energy of reactants is different from that of products, a reaction will occur. If it leads to a decrease in free energy, it will reach equilibrium when the free energy of the reactants and products becomes equal. For an explanation of the smelting and refining reaction, Gibb's energy (free energy at constant pressure) is used, which is calculated by using temperature, pressure, and concentration as independent variables. The reactions for smelting and refining are based on those of reduction and oxidation.

The figure shows the changes in the standard Gibb's energy which occur when oxides of elements are formed by the chemical reactions for producing iron and steel. This figure is called the Ellingham diagram. In general, the reaction in which an element reacts with 1 mole of oxygen to form an oxide is given by Eq. 1, and the change in the standard Gibb's energy of this reaction is given by Eq. 2, where G_0 is called the oxygen potential.

2B(1) Standard Free Energy of Formation of Oxides



Ref.: F.D.Richardson, JISI (1948)

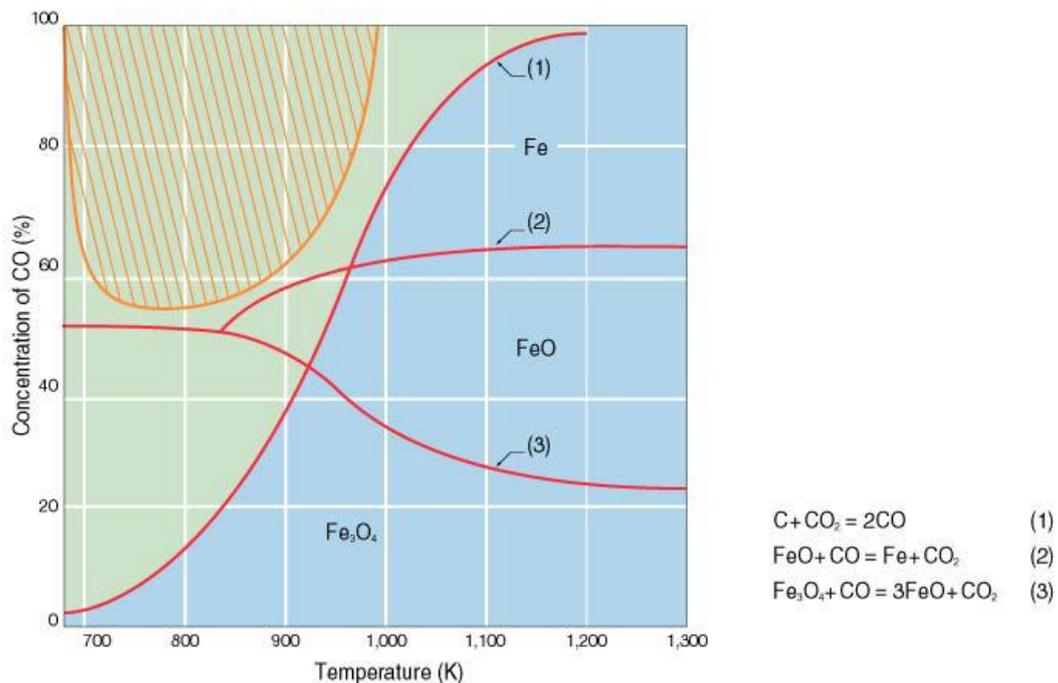
Taking an example of the reaction in which magnetite (Fe_3O_4) combines with oxygen to form hematite (Fe_2O_3), the Gibb's energy change at 1,000K during this reaction is about 200 kilojoules per 1 mole from the value at point A. When the straight line that connects point A with point Q is extrapolated to the line outside the right-hand margin, these two lines cross at a point where the partial pressure of oxygen (P_{O_2}) is about 10^{-6} Pascals (Pa). This shows that the reaction reaches equilibrium with a gas under an oxygen partial pressure of 10^{-6} Pascals (Pa) at 1,000K. In a gas with an oxygen partial pressure of higher than 10^{-6} Pascals (Pa), the reaction proceeds to form hematite. However, when the partial pressure of oxygen is lower than this level, hematite is decomposed and magnetite is formed; in other words, hematite is reduced to magnetite.

● Boudouard's Equilibrium

When reducing iron ore in the form of iron oxide by using solid carbon as the reducing agent, the carbon is oxidized into carbon monoxide and carbon dioxide.

The chemical reaction represented by Eq. 1 in the figure occurs among solid carbon, carbon monoxide and carbon dioxide.

2B(2) Equilibria among C, CO and CO₂ (Boudouard's Equilibrium)



Ref.: W. Baukloh et al., Arch. Eisenhüttenwes., (1940)

Curve 1 in the figure shows the equilibrium relationship for this reaction, which is called Boudouard's equilibrium. When the gas concentration of carbon monoxide is below this curve, the reaction proceeds in the direction for forming carbon monoxide, this being called the carbon solution reaction or solution-loss reaction. In the neighborhood of 1,200K, carbon dioxide that has been formed by the reduction of iron oxide is changed into carbon monoxide by this reaction, making

it possible to maintain the reducing capability of the gas. On the other hand, when the gas concentration of carbon monoxide is in the region above curve 1, a carbon deposition reaction occurs according to equilibrium theory; that is, carbon monoxide is dissociated into carbon dioxide and carbon, and carbon is deposited. However, due to its extremely slow speed, this reaction does not practically proceed at lower temperatures and low carbon monoxide concentrations. Carbon deposition actually occurs in the region where metallic iron coexists to provide strong catalytic action, and in the region of higher temperature and high carbon monoxide concentration. This region corresponds to the shaded part in the drawing. The figure also shows the regions of magnetite, wustite, and iron metal that coexist in a stable manner with carbon monoxide and carbon dioxide. It also shows that, at temperatures above 1,000K, reduction from magnetite to metallic iron can be achieved with a composition at which carbon monoxide and carbon dioxide are in equilibrium with each other.

Examination of the foregoing equilibrium theory makes it possible to decide whether a desirable reaction is possible and which conditions need to be met to obtain such a reaction. For practical control of a reaction, however, the mechanism that controls the reaction rate should be clarified and the heat and mass transfer should be analyzed on the basis of reaction rate theory and transport phenomena.

● Thermodynamic Quantities of Solutions

Various phases such as molten iron, slag, and gas are all involved in the smelting and refining of iron and steel. Although some of these phases may consist of a single substance or compound, they are in many cases a homogeneous phase composed of multiple components, namely a solution. The extensive quantities such as the free energy, enthalpy, and entropy of a solution undergo changes depending on the quantity and composition of the solution, as well as on its temperature and pressure. However, owing to interaction among the atoms of the solution components, the way in which change actually occurs is not as simple as when elements or compounds are mechanically mixed. Therefore, the partial molar quantity defined in Eq.1 is used to represent various thermodynamic relationships for the extensive quantities of the solution.

The suffixes for the partial differential coefficient in Eq.1 show that they are invariable. \bar{M}_i can be regarded as the amount of change in the quantity M when only component i is added in an extremely small quantity at a constant temperature and constant pressure, without changing the quantities of the other components. This is defined as the partial molar quantity of component i .

Among other partial molar quantities, the partial molar Gibb's energy is important in discussing the activity, etc. of a solution. It is called the chemical potential and is expressed by μ_i as shown in Eq. 2.

The difference between the partial molar quantity of a component of a solution and the quantity for the pure state of the component is referred to as the relative partial molar quantity of that component, and is expressed as Eq. 3.

Equilibrium of the chemical reactions related to a solution is governed by the activities of these reaction components. Therefore, knowledge of the activities of these components is necessary when considering the equilibria of reactions in smelting and refining and the reactivity of solution components. The activity of a solution component is defined in Eq. 4 as the ratio of the fugacity in the solution component to the fugacity in the standard state of that component (i.e., the ratio of the vapor pressures of the component when its vapor pressure is low).

The reference and standard state for activity can be arbitrarily selected. In general, the reference and standard state are adopted as shown in Eqs. 5-a, 5-b and 5-c for the smelting and refining of iron and steel. The figure shows the relationship between the activity and concentration of a solution component, A, B and C representing the standard state of activities in accordance with the respective reference states of Eqs. 5-a, 5-b and 5-c.

The relationship in Eq. 6 holds between the relative partial molar Gibb's energy and the activity of an actual solution component.

$$\left(\frac{\partial M}{\partial n_i}\right)_{T,P,n_1,\dots,n_{(i-1)},n_{(i+1)},\dots} \equiv \bar{M}_i \quad (1)$$

$$\mu_i = \bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,\dots,n_{(i-1)},n_{(i+1)},\dots} \quad (2)$$

$$\Delta \bar{M}_i \equiv \bar{M}_i - M_i^0 \quad (3)$$

$$a_i \equiv \frac{F_i}{F_i^0} = \left(\frac{P_i}{P_i^0}\right)_{ideal} \quad (4)$$

$$\lim_{N_i \rightarrow 1} \ln m_i(R) = N_i \quad (5-a)$$

$$\lim_{N_i \rightarrow 0} \ln m_i(H) = N_i \quad (5-b)$$

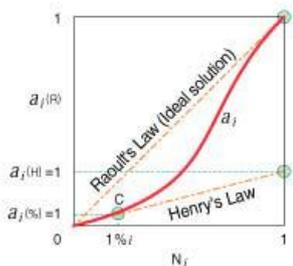
$$\lim_{\%i \rightarrow 0} \ln a_i = [\%i] \quad (5-c)$$

$$\Delta \bar{G}_i = RT \ln a_i(R) \quad (6)$$

$$\gamma_i = \frac{a_i(R)}{N_i} \quad (7-a)$$

$$\phi_i = \frac{a_i(H)}{N_i} \quad (7-b)$$

$$f_i = \frac{a_i(\%)}{[\%i]} \quad (7-c)$$



T : Temperature
 P : Pressure
 n : Number of Moles
 N : Mole fraction
 M : Extensive quantity of solution
 G : Gibb's energy of solution
 \bar{M}_i : Partial molar quantity
 \bar{G}_i : Partial molar Gibb's energy
 $\Delta \bar{M}_i$: Relative partial molar quantity
 $a_i(R)$: Activity referring to Raoult's Law
 $a_i(H), a_i(\%)$: Activity referring to Henry's Law
 F_i : Fugacity
 P_i^0 : Vapor pressure
 γ_i : Activity coefficient referring to Raoult's Law
 ϕ_i, f_i : Activity coefficient referring to Henry's Law

Subscript i refers to component i , and superscript o refers to the standard state.

The activity of a component in actual solution deviates from Raoult's law or Henry's law, and hence the activity coefficients defined by Eqs. 7-a, 7-b and 7-c are used to indicate the degree of the deviation.

For considering the activity and activity coefficient of the components in a multi-component solution, more detailed knowledge of the thermodynamics, such as interaction coefficients and interaction parameters, is required.

● Rates of Smelting and Refining Reactions

The various smelting and refining reactions involved in the iron and steelmaking processes generally proceed at high temperatures, so there are few cases where the chemical reaction rate controls the overall reaction rate. For example, the desulfurization of molten steel by slag shown in Eq. 1 is composed of the

elementary reactions given by Eqs. 2 and 3 and the associated reactions given by Eqs. 4, 5 and 6. It is known that these elementary and associated reactions are rate-controlled by mass transfer of the reactants in less than 1 second from the start of the reactions. As with decarburization, desulfurization and dephosphorization, when the overall reaction is rate-controlled by the reactant's mass transfer to the reaction interface, the change in the reactant's mole number "n" after time "t", i.e., the reaction rate "-dn/dt", can be expressed by Eq.7 as a function of area "A" of the reaction interface, mass transfer rate constant "k", the reactant's molar concentration "C", and equilibrium concentration "C_e".

2B(4) Rate of Smelting and Refining Reactions



Desulfurization reaction	$[S]_{\text{metal}} + (O^{2-})_{\text{slag}} = (S^{2-})_{\text{slag}} + [O]_{\text{metal}}$	(1)	
Elementary reactions	$[S]_{\text{metal}} + 2e = (S^{2-})_{\text{slag}}$	(2)	
	$(O^{2-})_{\text{slag}} = [O]_{\text{metal}} + 2e$	(3)	
Associated reactions	$[Fe]_{\text{metal}} = (Fe^{2+})_{\text{slag}} + 2e$	(4)	
	$[Mn]_{\text{metal}} = (Mn^{2+})_{\text{slag}} + 2e$	(5)	
	$[Si]_{\text{metal}} = (Si^{4+})_{\text{slag}} + 4e$	(6)	
Reaction rate	$-dn/dt = Ak(C - C_e)$	(7)	
Circulation flow rate of molten steel	$Q = V / \tau$	(8)	
Uniform mixing time	$\tau = \dot{\epsilon}^{-n}$	(9)	
Volumetric coefficient of mass transfer	$Ak \propto \dot{\epsilon}^n \quad (n = 0.3 \sim 0.4)$	(10)	

A : Interfacial area of reaction
 k : Mass transfer coefficient
 C : Molar concentration
 C_e: Equilibrium concentration
 V : Volume of molten steel
 τ : Uniform mixing time
 ε̇ : Stirring power density

To increase the rate "-dn/dt" of the overall reaction (the overall mass transfer rate), it is necessary to make "Ak" (the volumetric coefficient of mass transfer) large and

"Ce" small. The conditions for making "Ce" small are determined by a thermodynamic consideration. For any reaction of a gas/metal system or a slag/metal system, "Ak" can be made very large by blowing gas or slag into the metal bath or by enhancing the stirred flow and intermixing the slag and metal. The area "A" of the reaction interface increases markedly when gas is blown into the metal bath in a gas/metal system, and slag is blown into the metal bath (or metal is blown into the slag bath) in a slag/metal system; in such cases, the constant "k" also increases at the same time because of the stirring of slag or metal which accelerates the transfer of the reactants to the reaction interface.

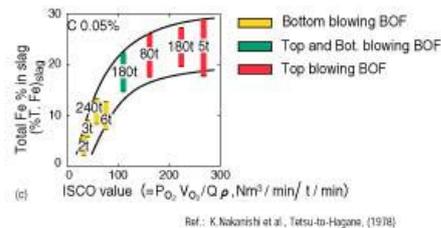
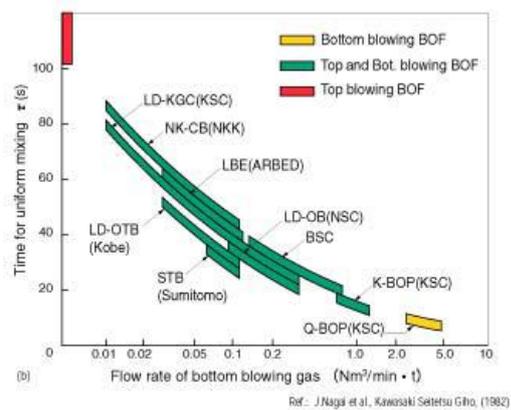
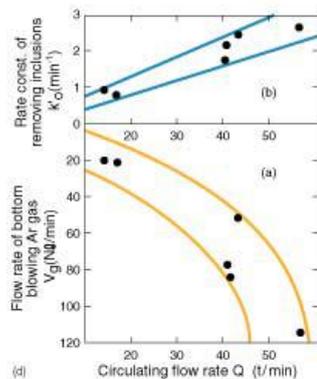
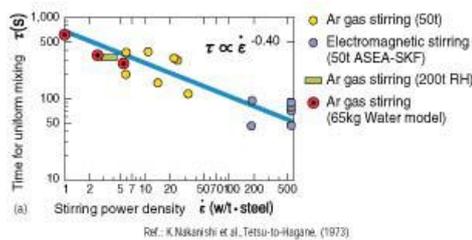
Taking a molten steel bath of volume "V" as an example, it is conceivable that the rate at which the reactants in the bath reach the reaction interface is proportional to circulating flow rate "Q" of the molten steel in the bath. The rate "Q" is related by Eq. 8 to the uniform mixing time "", which refers to the time necessary for the reactants to disperse uniformly in the bath. Time "" is related by Eq. 9 to the stirring power density "", which refers to the power of stirring applied per unit weight or volume of the bath. In the refining reactions for a gas/metal system and slag/metal system, there are many cases in which Eq. 10 can be applied, even when the power for stirring is applied in different manners, such as by gas blowing, electromagnetic induction, or mechanical rotation. The reason why "n" takes the value of 0.3-0.4 has been explained for the respective stirring method in terms of transport phenomena. However, "n" may sometimes reach 0.4-1.0 when ""

increases further and metal particles disperse into the gas or slag, or gas bubbles and slag particles disperse into metal.

As in the example for the rate of ore reduction by gas flowing through the charged layers of coke and ore in a BF, research on the solid phase reaction rate has also progressed to such an extent that ore reduction can be treated as the problem of a migrating boundary layer, and analysis is made by linking the ascent of the gas with the heat and mass transfer caused by the descent of lump ore and coke into the lower shaft of the BF.

● Stirring of Steel Bath, Circulating Flow Rate and Mass Transfer Rate

2B(5) Stirring of Steel Bath, Circulating Flow Rate and Mass Transfer Rate



Figure(a) shows that an increase in stirring power density applied to the steel bath intensifies circulation of the molten steel and reduces the uniform mixing time. Regardless of the stirring method employed, the relationship shown in this figure holds true, and the time required for uniform mixing can be reduced by as much as one order of magnitude if molten steel is stirred at 200 W/ton. How much the overall mass transfer rate increases with increased stirring of the steel bath and an increased circulating flow rate is shown next by several examples. Figure(b) shows a case in which the uniform mixing time was significantly reduced by blowing gas into the steel bath from the furnace bottom of the BOF. When t is short and the circulating flow rate Q of the molten steel is high, the mass flux of carbon transferred to the zone where oxygen gas comes into contact with the steel bath also becomes large. Therefore, the mass transfer rate of carbon increases, carbon is preferentially oxidized and decarburized, and the degree of oxidization of molten steel due to the formation of iron oxide and of iron loss in the slag becomes low. This advantage is especially great when the target carbon content becomes low, as shown in Fig.(c). The index used in this figure is the value obtained by dividing the product of partial pressure P_{O_2} of oxygen in the furnace and oxygen volume V_{O_2} supplied per unit time to the reaction interface (mass flux of oxygen) by the product of circulating flow rate Q of the molten steel and specific weight r of the molten steel (corresponding to the mass flux of carbon). This index is called the ISCO value (index for selective carbon oxidation).

The value τ in a top-blown BOF is a little more than 100 seconds in Fig.(b), while the ISCO value corresponding to this value τ is about 230 in Fig.(c). The value τ in bottom-blown BOF is about 12 seconds, and the corresponding ISCO value is about 60. As shown in Fig.(c), with τ decreasing from a little more than 100 seconds to 12 seconds and the corresponding ISCO value decreasing from 230 to 60, the iron oxide in slag that is formed by oxidation of steel decreases substantially from about 23% to 10% as the total iron content. As a result of stirring, shorter (higher Q), that is, a lower ISCO value, will result in a higher overall mass transfer rate of carbon for the oxidation, and hence smaller oxidation loss of molten steel, giving higher iron yield.

The relationship that the overall mass transfer increases substantially with increasing Q or $1/\tau$ holds true not only for the decarburization that occurs between gas and metal, but also for the dephosphorization and desulfurization that occur between slag and metal. Furthermore, this relationship also holds true for the deoxidation that removes oxide inclusions such as alumina formed and suspended in the steel bath after adding a suitable deoxidizing agent such as aluminum. The result of bottom-blowing argon gas into the aluminum-killed stainless steel bath in a vacuum oxygen decarburization (denoted VOD hereinafter) furnace is shown in Fig.(d) as an example of this. When the bottom-blown gas flow rate was increased from 20 to 70 N/min, Q increased from 10 to 40 ton/min and, as a result, the mass transfer coefficient for alumina inclusion removal

(deoxidation) was doubled from 1 to 2/min. Vortices are generated by stirring molten steel, and due to the velocity gradient in the vortices, inclusions collide with each other, coalesce, and become large. When their critical diameter is exceeded, these inclusions float outside of the system. Higher Q and higher result in a higher value of k, because the number of vortices and the velocity gradient in the vortices both increase.

These various blowing and stirring operations are used for smelting and refining reactions and, as a result, remarkable progress has been achieved in the iron and steelmaking processes. This procedure has been developed to the extent that a region of high oxygen potential and low temperature is intentionally formed in one part of a reactor, a region of low oxygen potential and high temperature is intentionally formed in another part, and dephosphorization and desulfurization are simultaneously promoted in the former and latter regions, respectively. This technique has been put into practical use as a simultaneous dephosphorization and desulfurization process for pretreating hot metal and has substantially reduced the dephosphorization and desulfurization load in BOF blowing.

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