

Solution:

(a) From Eq. (20.2), $P = \frac{340QT}{M} \ln \left(1 + \frac{0.707H}{P_0} \right)$

Here, $\frac{Q}{M} = 0.1 \times \frac{1}{60}$, $T = 1900$ K, $H = 1$ m, $P_0 = 1$ bar (assumed).

Inserting these values in Eq. (20.2), $P = 576$ watts/tonne of steel.

(b) $t_{\text{mix}} \propto P^{-m} \propto Q^{-m}$. Noting that $m = \frac{1}{2}$, $\frac{(t_{\text{mix}}) \text{ at } 0.2 \text{ Nm}^3}{(t_{\text{mix}}) \text{ at } 0.1 \text{ Nm}^3} = 2^{-1/2}$.

Hence, t_{mix} at $0.2 \text{ Nm}^3/\text{min/t} = 60 \times 2^{-1/2} = 42.4$ s.

20.3 DEOXIDATION OF LIQUID STEEL

In Chapter 15, Sections 15.4.1–15.4.4 the reaction of oxygen dissolved in the bath with Fe, Mn, C and Si has been discussed. Equilibrium relations were presented. Solubility of oxygen in molten iron in equilibrium with FeO also has been indicated there. It was mentioned that the turndown oxygen level in BOF steelmaking typically ranges between 600 and 1000 ppm, and is much higher than even for Fe-[O]-(FeO) equilibrium. In Chapter 17, Section 17.7, some empirical correlations have been presented between dissolved carbon and oxygen in metal bath with slag FeO, MnO, etc.

Solubility of oxygen in solid steel is negligibly small. Therefore, during solidification of liquid steel, the excess oxygen is rejected by the solidifying metal. This excess oxygen causes defects by reacting with C, Mn, Si, etc. resulting in the formation of blowholes (primarily CO) and oxide inclusions (FeO–MnO, SiO₂, Al₂O₃, etc.). Evolution of CO has a significant influence on the structure and homogeneity of the cast metal as well. Therefore, dissolved oxygen levels in molten steel have to be lowered by the addition of strong oxide formers, such as Mn, Si, Al, Ca (as ferromanganese, ferrosilicon, silico-manganese, aluminium, calcium silicide) in the ladle. This is known as deoxidation.

Chapter 18 has elaborated the fundamentals and application of immersion-type oxygen sensors for process control. They are used to determine the concentration of oxygen dissolved in molten steel very quickly. Similar sensors have been employed in the laboratory extensively, and also in secondary steelmaking to assess the extent of deoxidation.

20.3.1 Thermodynamics of Deoxidation of Molten Steel

A deoxidation reaction may be represented as:



where M denotes the deoxidiser (Mn, Si, Al, etc.), and M_xO_y is the deoxidation product. The equilibrium constant for reaction (20.3) is given as

$$K_{M'} = \left\{ \frac{(a_{M_xO_y})}{[h_M]^x [h_O]^y} \right\}_{\text{eq.}} \quad (20.4)$$

If the deoxidation product is a pure oxide (SiO_2 , Al_2O_3 , etc.), then $a_{\text{M}_x\text{O}_y} = 1$. Since wt. % M and O in steel are generally very low, h_M and h_O may be taken as their wt. percentages respectively (i.e. W_M and W_O). [Note: If this assumption is not made, then h_M and h_O are to be related to W_M and W_O through interaction coefficients as per the procedure given in Chapter 4, Section 4.3.4.] Then, Eq. (20.4) may be simplified as:

$$\left\{ [W_M]^x [W_O]^y \right\}_{\text{eq.}} = \frac{1}{K_M'} = K_M \quad (20.5)$$

where K_M is known as the *Deoxidation Constant*. Variation of K_M with temperature has the form:

$$\log K_M = -\frac{A}{T} + B \quad (20.6)$$

where A and B are constants, which can be calculated from data available in literature. Table 20.2 presents typical K_M values for some common deoxidisers. The wt. % [O] in equilibrium with 0.1 wt. % M at 1600°C (1873 K) are respectively 0.413, 0.0145, 1.35×10^{-3} and 9.84×10^{-10} for Mn, Si, Al and Ca. According to this, calcium is the strongest and manganese the weakest amongst the deoxidisers. Si is stronger than Mn and Al is stronger than Si. This follows directly from the Ellingham Diagram for oxides (Figure 4.1) showing the relative stabilities of some oxides.

Table 20.2 Values of K_M for some deoxidisers

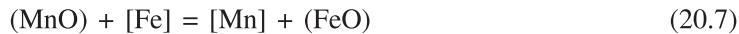
Deoxidant (M)	Deoxidation product	Concentration range of M(W_M), if any	$\log_{10} K_M$	K_M at 1873K
Al	Al_2O_3	above 10^{-5}	$-\frac{64000}{T} + 20.57$	2.51×10^{-14}
C	CO (g)		$-\frac{1160}{T} - 2.003$	2.39×10^{-3}
Ce	Ce_2O_3		$-\frac{68500}{T} + 19.6$	10^{-17}
Cr	FeCr_2O_4	below 3.0	$-\frac{45796}{T} + 18.83$	2.39×10^{-6}
	Cr_2O_3	3.0–8.0	$-\frac{45531}{T} + 20.25$	8.72×10^{-5}
	Cr_3O_4	above 8.0	$-\frac{48850}{T} + 21.45$	2.23×10^{-5}
Mn	FeO–MnO (l) solution	below 0.2	$\log K_{\text{Mn}} = -\frac{6440}{T} + 2.93$	0.3102
			$\log K_{\text{Mn-Fe}} = -\frac{6525}{T} + 2.948$	0.29
	FeO–MnO (s) solution	above 0.2	$\log K_{\text{Mn}} = -\frac{6990}{T} + 3.01$	0.19

(Contd.)

Table 20.2 Values of K_M for some deoxidisers (Contd.)

Deoxidant (M)	Deoxidation product	Concentration range of $M(W_M)$, if any	$\log_{10} K_M$	K_M at 1873K
			$\log K_{\text{Mn-Fe}} = \frac{6980}{T} + 2.91$	0.15
Si	SiO_2		$-\frac{30110}{T} + 11.4$	2.11×10^{-5}
Ti	Ti_3O_5	0.0004–0.4	$-\frac{90727}{T} + 29.15$	5.45×10^{-20}
	Ti_2O_3	above 0.4	$-\frac{55751}{T} + 17.90$	2.06×10^{-12}
Ca	CaO		$-\frac{32903}{T} + 7.56$	9.84×10^{-11}
Mg	MgO		$-\frac{32027}{T} + 8.47$	2.35×10^{-9}

When only one deoxidiser is added, it is known as a *Simple Deoxidation*. Mostly, a single oxide is formed as the product, except for mild deoxidisers, such as Cr and Mn, where the product is typically a slag $\text{FeO}-\text{Cr}_2\text{O}_3$ or $\text{FeO}-\text{MnO}$. For example, for deoxidation by Mn, the more appropriate equation is:



for which

$$K_{\text{Mn-Fe}} = \frac{[h_{\text{Mn}}] \times (a_{\text{FeO}})}{(a_{\text{MnO}})} = \frac{[W_{\text{Mn}}] \times (X_{\text{FeO}})}{(X_{\text{MnO}})} \quad (20.8)$$

where X is mole fraction, since, both $\text{Fe}-\text{Mn}$ and $\text{FeO}-\text{MnO}$ solutions are ideal.

If more than one deoxidiser is added to molten steel simultaneously, it is known as *Complex Deoxidation*. Some important complex deoxidisers are $\text{Si} + \text{Mn}$, $\text{Si} + \text{Mn} + \text{Al}$, $\text{Ca} + \text{Si}$, $\text{Ca} + \text{Si} + \text{Al}$. For this, the deoxidation product is a slag consisting of more than one oxide. Therefore, for thermodynamic analysis, activity vs. composition relationships in oxide solutions (for example, $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$ system, as shown in Figure 4.3) has to be considered. Generally, this requires the development of elaborate computer programmes with the aid of numerical techniques. Commercial packages (e.g. FACTSAGE) are available. For details, readers may refer to the paper (Choudhary et al. 2005).

EXAMPLE 20.2

Calculate the dissolved oxygen content of liquid steel containing 0.1% Si at equilibrium with solid SiO_2 at 1600°C.

Given: $e_{\text{Si}}^{\text{Si}} = 0.103$, $e_{\text{Si}}^{\text{O}} = -0.113$, $e_{\text{O}}^{\text{O}} = -0.20$, $e_{\text{O}}^{\text{Si}} = -0.066$

Solution: For the deoxidation reaction: $[Si]_{wt.\%} + 2[O]_{wt.\%} = SiO_2(s)$, from Table 20.2,

$$K_{Si} = [h_{Si}] \times [h_O]^2 = 2.11 \times 10^{-5} \quad (\text{Ex. 20.1})$$

i.e.

$$[f_{Si} \cdot W_{Si}] \times [f_O \cdot W_O]^2 = 2.11 \times 10^{-5}$$

or

$$\log f_{Si} + \log W_{Si} + 2(\log f_O + \log W_O) = \log (2.11 \times 10^{-5}) \quad (\text{Ex. 20.2})$$

$$\log f_{Si} = e_{Si}^{Si} \cdot W_{Si} + e_{Si}^O \cdot W_O = 0.103 \times 0.1 - 0.113 \times W_O$$

$$\log f_O = e_O^O \cdot W_O + e_O^{Si} \cdot W_{Si} = -0.20W_O - 0.066 \times 0.1$$

Combining all these in Eq. (Ex. 20.2), it is possible to get:

$$2 \log W_O - 0.64W_O = -3.649 \quad (\text{Ex. 20.3})$$

Eq. (Ex. 20.3) requires iterative procedure for solution. By trial and error, $[W_O] = 0.019$ wt. %.

20.3.2 Kinetics of Deoxidation of Molten Steel

Fundamental studies on deoxidation kinetics have been generally conducted in laboratory induction furnaces, and it may be subdivided into the following.

1. *Kinetics of deoxidation*, consisting of dissolution of deoxidisers into molten steel, chemical reaction between dissolved oxygen and the deoxidising element, nucleation and initial growth of the deoxidation product. The process is fast and gets completed in a minute or two.
2. *Kinetics of elimination of deoxidation products from liquid steel*, consisting of further growth of deoxidation products by agglomeration and their elimination from liquid steel; this is a slow process and is thus rate-limiting.

Figure 20.5 shows the change in the oxygen and inclusion content of steel from the tapping to the solidification stage, deoxidisers being added when steel is tapped into the ladle from the primary steelmaking furnace (Plockinger and Wahlster, 1960). The dissolved oxygen content as measured by an immersion oxygen sensor, decreases rapidly indicating the fast reaction kinetics. The *total oxygen content* is determined by collecting samples of molten steel and analysing the sample in a vacuum/inert gas fusion apparatus. It includes the oxygen in the oxides formed as deoxidation products as well. As shown in the Figure, the total oxygen is much higher than the dissolved oxygen, since the elimination of inclusions from liquid steel takes a long time.

The oxide products are lighter than liquid steel and are removed following floatation to the top of the melt. *Stokes' Law of Settling* applicable for *laminar flow*, is often used as a guide. It relates the *terminal velocity* of the particle (v_t) with some physical variables as:

$$v_t = \frac{gd^2(\rho_l - \rho_s)}{18\eta} \quad (20.9)$$

where g is acceleration due to gravity, d is the particle diameter, η is the viscosity of the liquid, ρ_l and ρ_s are densities of liquid steel and solid oxide respectively.

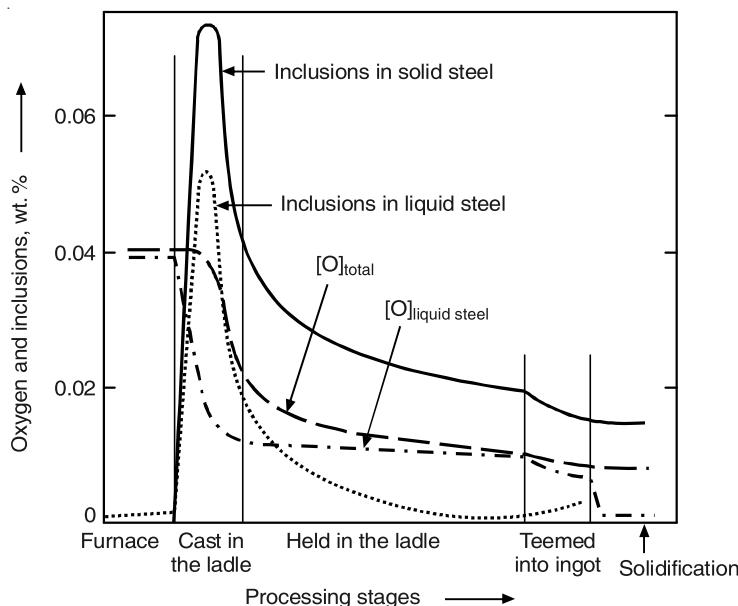


Figure 20.5 Change of oxygen and inclusion content of steel between tapping and solidification.

Since $v_t \propto d^2$, the larger particles float-up much faster than the smaller particles. Deoxidation products grow by collision and agglomeration. Collision of small particles is speeded up by turbulence. Agglomeration is better if the particles are liquid. This is where complex deoxidation has a significant advantage, since the product can be a liquid slag particle.

Turbulence also speeds up flotation of the solid particles. Inert gas purging in the ladle is, therefore, very beneficial as an aid to produce clean steel. This has been well-established through both laboratory and plant-scale experiments. The total oxygen content $[W_O(T)]$ at any time after deoxidiser addition may be approximately related to time by:

$$W_O(T) = [W_O(T)]_{\text{initial}} \cdot \exp(-k_O t) \quad (20.10)$$

where k_O is an empirical constant.

It increases with the increase in bottom gas flow rate, i.e. specific stirring power (P) as

$$k_O \propto P^n, \quad \text{where } n < 1 \quad (20.11)$$

However, trials in industrial ladles have established that there is an optimum stirring intensity beyond which, the effectiveness of deoxidation decreases, as shown in Figure 20.6 (Suzuki et al. 1982). This is because the flow in ladles is re-circulatory (see Figure 20.3), and excessive stirring causes re-entrainment of the floated oxides back into the melt. It also causes more oxidation by air. Actually, from a more rigorous point of view, the final degree of deoxidation achieved is a dynamic balance between the rate of elimination of the oxide particles on one hand, and the rate of atmospheric oxidation on the other.

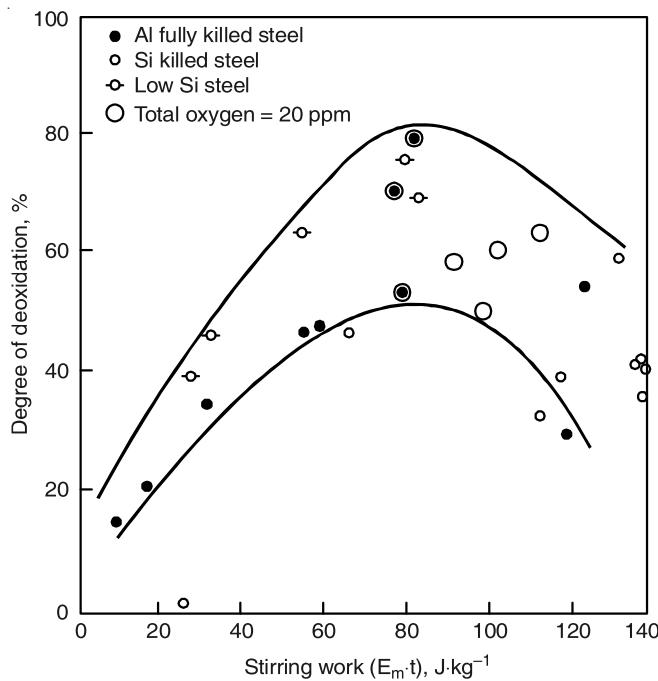


Figure 20.6 Effect of stirring on the degree of deoxidation.

20.3.3 The Ladle Furnace (LF)

Figure 20.7 shows the sketch of a ladle furnace. The ladle with liquid steel is brought to the LF station, where a top cover is placed on the ladle and graphite electrodes are introduced. It is the most commonly used unit in secondary steelmaking. In the LF, deoxidation and composition adjustments are carried out by additions, and the temperature of the melt is adjusted by arc heating. Bath stirring is achieved by means of argon purging from the bottom. The top cover gives significant protection from atmospheric oxidation, but is not completely sealed and some ingress of air is inevitable.

In the LF, besides deoxidiser and alloying additions, the slag is primarily modified by the addition of CaO, and sometimes by CaF₂ as well. The slag is basic, and its typical composition range is 50 to 56% CaO, 7 to 9% MgO (coming from burnt dolomite lining), 6 to 12% SiO₂, 20 to 25% Al₂O₃, 1 to 2% (FeO + MnO), 0.3% TiO₂ and occasionally some amount of CaF₂. The Al₂O₃, and to some extent SiO₂, are products of deoxidation by Al and Si. Percentages of utilisation of ladle additions for low carbon heats are 80 to 95% for Mn, 50 to 70% for Si, and 30–65% for Al. Aluminium is costly, and hence its poor utilisation is a matter of concern. In order to improve it, the modern practice is to go in for aluminium wire feeding instead of addition as ingots or cubes.

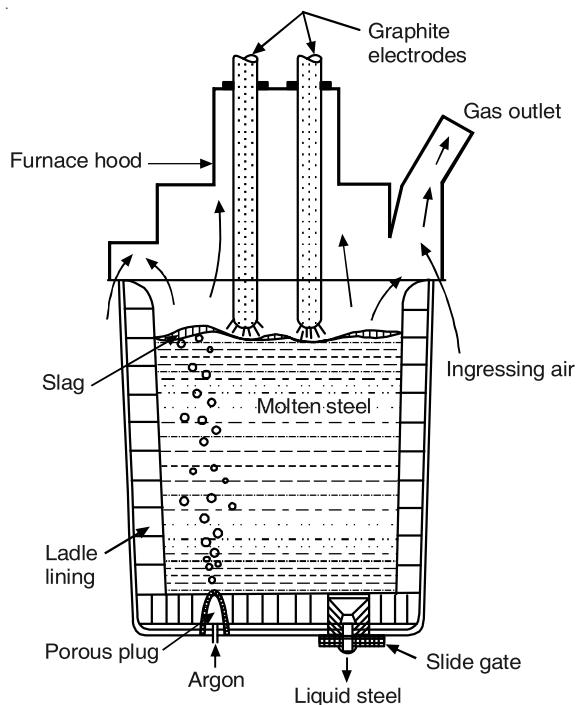


Figure 20.7 Sketch of a ladle furnace.

20.3.4 Problem of Slag Carryover

The primary steelmaking slag has a high percentage of iron oxide (see Section 15.3). A portion of this slag comes into the ladle during tapping because of *slag carryover*. Owing to its high iron oxide content, a significant quantity of deoxidiser is consumed by it. Another serious problem is what is known as *Phosphorus Reversion* in ladles from slag to metal. High concentration of iron oxide in slag is a major factor for the retention of phosphorus in slag. Deoxidation of slag, therefore, tends to transfer phosphorus back from slag into metal. Therefore, modern steel melting shops aim at *slag-free tapping*; however, complete prevention of slag carryover is seldom achieved and minimisation becomes the objective.

Formation of a funnel-shaped gas core during emptying of liquid from a vessel (such as a kitchen sink) is a common experience. During tapping of liquid steel from a BOF or any other furnace, or teeming from the ladle or tundish into the continuous casting mould, such a funnel causes the top slag to flow out along with the metal, towards the end when the liquid metal level is very low. Some fundamental studies have been conducted on this phenomenon in water models (Shankarnarayanan and Guthrie, 1992).

For minimising slag carryover, a plug-shaped refractory piece, known as a *dart*, is dropped into the converter towards the latter stages of tapping. Its density is in between that of slag and metal, which makes it float between the metal and slag layers. When it gets dragged into the funnel owing to vortex formation, it blocks the nozzle and significantly prevents slag carryover. In electric furnaces, eccentric bottom tapping is practiced to minimise slag carry over.

Another device that is useful in reducing slag carryover is an *electromagnetic sensor*, which is placed around the tap hole. When the slag starts flowing out through the tap hole nozzle, the nature of the signal changes significantly because of the differences in electromagnetic induction of slag and metal. This device is considered to be very effective. In plant trials with 130/140 t BOF converters at Linz, the following average slag rates (in kg of slag per tonne steel) were obtained:

- Without slag stopper 10–15
- With slag stopper 4.45
- With slag stopper and slag indication 3.5

20.3.5 The CAS-OB Process

The important features of the CAS-OB process are shown in Figure 20.8. It has been developed by Nippon Steel Corporation of Japan. CAS stands for Composition Adjustments by Sealed argon bubbling. Following this treatment, the losses by oxidation of deoxidisers and alloys is low. The dissolution becomes faster because of high turbulence and stirring at the plume eye. With additional facilities for oxygen blowing, the temperature can be raised because of exothermic heat supplied by aluminium oxidation. As a result, arc heating is not required. The process has the advantage of low capital cost and several steel plants around the world have installed it.

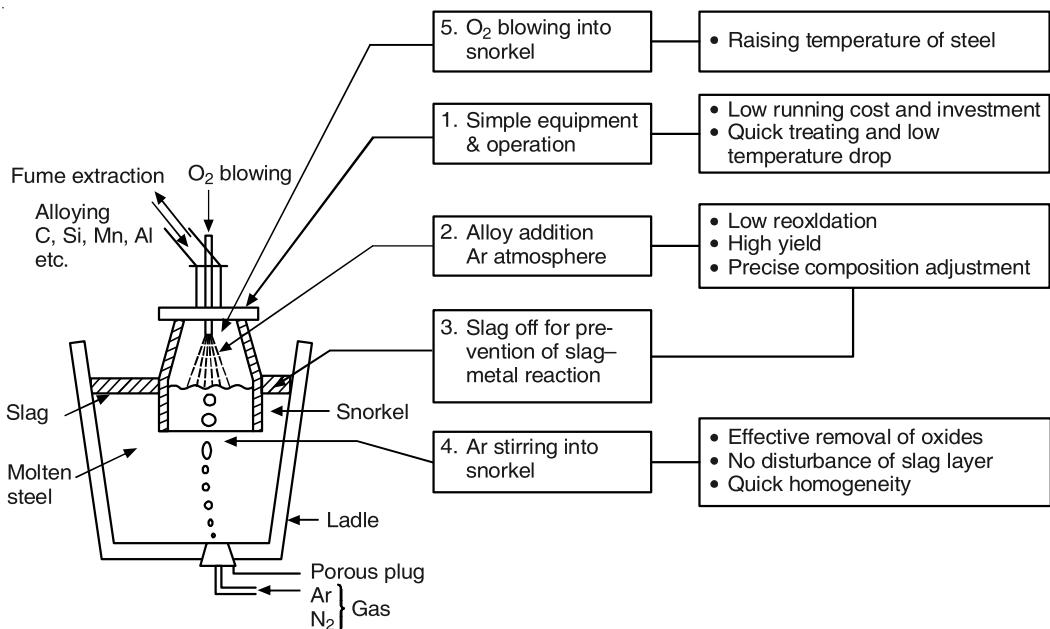


Figure 20.8 Salient features of the CAS-OB process.