

so as to make them relatively harmless as far as the properties of steel are concerned. This is done by injection metallurgy, and again, calcium is the most common reagent. Section 20.5.3 has already discussed this in connection with desulphurisation. These will not be repeated.

One of the defects in continuous casting is formation of *subsurface pinholes* owing to the presence of dissolved gases. Therefore, the oxygen content of the melt should be kept very low by use of aluminium also as deoxidiser (Al-killed steel). A certain minimum level of dissolved Al is required in the melt. This gives rise to the problem of nozzle clogging in continuous casting owing to sticking of alumina inclusions to the inner wall of the casting nozzle. Calcium treatment at the final stage in a ladle or a tundish has been found to eliminate this, because the deoxidation product is a liquid consisting of CaO and Al_2O_3 , occasionally with some amount of SiO_2 .

Calcium is a powerful desulphuriser as well, and therefore, reaction (20.16) resulting in the formation of CaS also may occur. However, the liquid sulphide is generally not pure CaS, but a solution of CaS–MnS. The compounds $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (C_{12}A_7) and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (C_3A) have low melting points of 1455°C and 1535°C respectively, and therefore, are preferred.

Figure 20.18 shows thermodynamic predictions for equilibrium inclusion type for calcium-treated steels as a function of its Al and S content at 1550°C (1823 K), assuming CaS to be pure (Fruehan 1985). Although originally Ca-treatment was started to overcome problems of nozzle-clogging, the duplex inclusion of (C_{12}A_7) with a ring of CaS–MnS is globular, soft and deformable, and thus relatively harmless to mechanical properties.

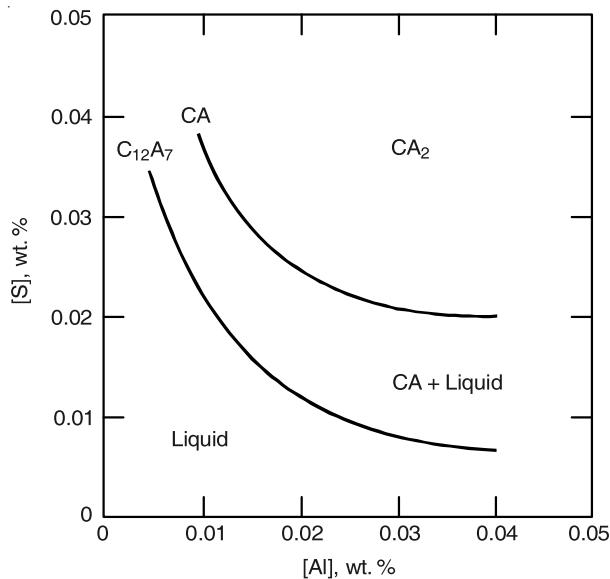


Figure 20.18 Equilibrium inclusions predicted for calcium-treated Al-killed steels, as function of Al and S content at 1823 K.

Rare earths (RE) consist of 14 elements having almost identical chemical properties. Commercially it is available as *Misch metal*, which contains about 50% cerium. REs are both strong deoxidisers and desulphurisers, like calcium. They can modify inclusions as well as act as grain refiners. However, they are not as commonly used as calcium because of difficulties of

process control. Tellurium (Te) or Selenium (Se) is also added as a reagent for inclusion modification to improve the machinability of sulphur containing steels. Their basic effect is to make the inclusions globular, thus leading to better deformation characteristics during hot working as well.

20.7.2 Temperature Changes during Secondary Steelmaking

For obtaining the desired cast structure as well as for elimination of some casting defects, the temperature of liquid steel should be controlled within a desired range before it is teemed into the mould. Continuous casting demands more stringent temperature control than ingot casting.

In secondary steelmaking, the temperature may drop by as much as 100°C from the furnace to the mould. Therefore, some secondary steelmaking units, such as LF, VAD and RH have provisions for heating the melt. Pre-heating of the lining of empty ladle is also standard practice so that the interior hot face lining temperature is above 800°C. These measures eliminate the need for tapping at too high a temperature. Moreover, much better and more flexible temperature control of steel is then possible. More alloy additions also can be made. Arc heating is most common, followed by chemical heating, plasma arc or induction heating for reducing the temperature loss during secondary treatment. Chemical heating requires aluminium addition as well as some oxygen lancing, as is the case in RH–OB. Exothermic oxidation of aluminium provides the heat.

The overall temperature change of liquid steel from the furnace to the mould is a sum total of the following:

- Temperature loss from the tapping and teeming stream by radiation and convection
- Temperature loss during holding or purging in the ladle because of conduction to the ladle wall and radiation from the top surface of the melt
- Temperature loss owing to endothermic dissolution of deoxidants and alloying elements added at room temperature
- Temperature gain following exothermic deoxidation reactions (also, atmospheric re-oxidation)
- Temperature gain on account of heating.

Figure 20.19 shows a typical pattern of temperature change from the furnace to the continuous casting mould via the ladle furnace route (Mellinghoff 1991). The estimated decrease in steel temperature during tapping for 1% alloying element addition and assuming 100% recovery (i.e. no reaction) is as follows.

Addition	Decrease in steel temperature, °C
Coke	65
High carbon ferrochrome (50% Cr)	41
Low carbon ferrochrome (70% Cr)	24
High carbon ferromanganese	30
Ferrosilicon (50% Si)	0

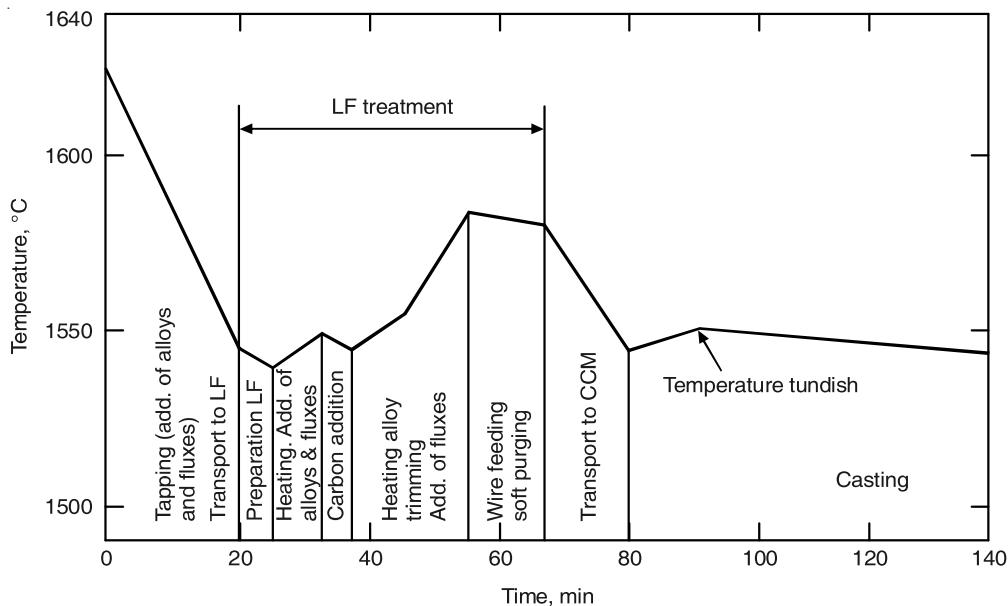


Figure 20.19 Temperature changes in a steel melt from the furnace to the tundish via ladle furnace.

EXAMPLE 20.5

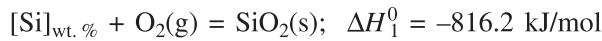
Calculate the change in temperature (ΔT) of 150 tonne of molten steel in a ladle at 1600°C following the addition of 70 kg of ferrosilicon having 50% Si. Assume that half of the silicon reacts with dissolved oxygen of steel, and the rest remains dissolved in steel.

Solution: $70/2 = 35 \text{ kg Si} = (35 \times 10^3)/28 = 1.25 \times 10^5 \text{ gmol of Si}$

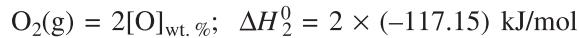
Assuming steel to be pure iron,

$$150 \text{ tonnes of steel} = (150 \times 10^6)/56 = 2.68 \times 10^6 \text{ gmol}$$

From Chapter 15, Table 15.1,



The first column of Table 4.2 of Chapter 4 gives values of ΔH^0 approximately and, from that



From the above reactions,

$$[\text{Si}]_{\text{wt. \%}} + 2[\text{O}]_{\text{wt. \%}}; \quad \Delta H^0 = \Delta H_1^0 - \Delta H_2^0 = -581.9 \text{ kJ/mol} \quad (\text{Ex. 20.8})$$

Again, from Table 4.2,

$$\bar{H}_{\text{Si}}^m \text{ owing to dissolution of silicon into the melt} = -131.5 \text{ kJ/mol.}$$

Heat Balance:

Since the above processes are exothermic, they are the sources of heat input. Since, only half of the silicon added reacts with dissolved oxygen,

$$\text{Heat input} = -1.25 \times 10^3 \times \{0.5 \times [-581.9] + [-131.5]\} = 5.28 \times 10^5 \text{ kJ}$$

Assuming the process to be adiabatic,

Heat output = Heat required to raise the steel temperature by ΔT + Sensible heat required to raise the temperature of ferrosilicon from 298 K to 1873 K

Noting that $(H_{1873} - H_{298})$ for Fe and Si are respectively 76.94 and 33.5 kJ per gmol, the sensible heat of Fe-Si addition = $10^3 \times [1.25 \times 33.5 + (0.5 \times 70 \times 76.94)/56] = 0.9 \times 10^5 \text{ kJ}$

From Table 15.2, ignoring the T^2 term, raising of steel temperature would require heat.

No. of gmol of steel $\times 40.9 \times \Delta T = 2.68 \times 10^6 \times 40.9 \times \Delta T \times 10^{-3} = 1.10 \times 10^5 \times \Delta T \text{ kJ}$
So, heat output (in kJ) = $1.10 \times 10^5 \times \Delta T + 0.9 \times 10^5$

Equating heat input and output, $\Delta T = 4.0^\circ\text{C}$

20.7.3 Refractories for Secondary Steelmaking

In contrast to primary steelmaking, the slag in secondary steelmaking is deoxidised and contains a high proportion of CaO and Al₂O₃. In primary steelmaking, the choice and design of the refractory lining is governed by the lining life and its impact on the overall steelmaking cost. However, in secondary steelmaking, there are additional concerns about its effect on steel quality, cost of ladle heating, etc. The requirements of the refractory lining for secondary steelmaking ladles are given below.

1. The lining should be stable as well as inert to liquid steel. Otherwise, it will tend to introduce undesirable impurities into the metal.
2. A low thermal conductivity of the ladle lining is desirable to prevent heat loss by conduction through the walls. However, thermal shock resistance should also be satisfactory. Often these are contrary requirements and a balance has to be struck.
3. Steel cleanliness, to some extent, depends on the interaction between liquid steel and the refractory lining. Erosion of the lining increases the number of exogenous nonmetallic particles, whereas corrosion causes a change in the composition of steel, like increasing its oxygen content. This, in turn, tends to generate more deoxidation products during freezing of steel in the mould.

Nowadays, tar or pitch bonded calcined dolomite (CaO.MgO) lining is generally employed as the ladle lining. For clean steel, it should have high purity (total impurity less than 3% or so). Composite linings are normally used. The zone in contact with the top slag has to resist slag attack adequately and calcined dolomite serves the purpose. To reduce the weight, expense and total heat capacity of the refractory system, a fireclay back up lining is provided.

Ladle covers are typically lined with high-alumina refractories (above 85% Al₂O₃). Porous plugs are made of high alumina or magnesia. Slide gate parts undergo high stresses and are generally made from high alumina material. The refractory lining for teeming nozzles has already been discussed in Section 20.6.3.

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21

Stainless Steelmaking

21.1 INTRODUCTION

Amongst high alloy steels, stainless steels (SS) are the most important. The world production of SS is about 20 Mtpa. Therefore, stainless steels production is being dealt with in this separate chapter.

Stainless steels contain 10 to 30% chromium. Varying amounts of nickel, molybdenum, copper, sulphur, titanium, niobium, nitrogen, etc. may be added to obtain the desired properties. SS is used wherever superior resistance to corrosion is desired. Stainless steels are primarily classified as *austenitic*, *ferritic*, *martensitic*, duplex or precipitation hardening grades. Most grades contain 17–18% chromium. Addition of nickel enhances the corrosion resistance further and tends to stabilise the austenitic structure—the most popular SS is the 18% Cr and 8% Ni variety.

In terms of tonnage production, ferritic SS is next. Production of ferritic SS requires the removal of carbon and nitrogen in steel to very low levels. Nickel, which is an integral part of stainless steels is expensive and efforts have been made from the 1950s to replace it, partially or completely, by other elements, such as manganese, which tend to stabilise the austenite phase. However, this can be achieved more easily, if the steel contains high percentages of nitrogen (0.06–0.08%); high nitrogen SS grades are being produced today.

Before 1970, the majority of stainless steels were made in electric arc furnaces. In Chapter 19, the application of EAF steelmaking for producing carbon steel grades has been covered along with the modern developments. Availability of relatively cheap tonnage oxygen led to the practice of oxygen lancing for faster decarburisation and the consequent generation of a foamy slag. This development changed the entire picture.

Owing to rapid growth in SS production from about 1970 onwards, the generation/supply of SS scrap could not meet the demand and other charge materials had to be used. The quantities of various charge materials that are now used are as follows (based on 2001 figures):

Carbon steel scrap	7.0 Mt
Stainless steel scrap	4.5 Mt
Ferrochrome	4.0 Mt
Primary nickel	0.7 Mt

Ferrochrome, which contains about 55 to 70% chromium is the principal source of chromium. This ferroalloy can be classified into various grades, based primarily on their carbon content, such as:

- Low carbon ferrochrome (about 0.1% C).
- Intermediate carbon ferrochrome (about 2% C).
- High carbon ferrochrome (around 7% C).

Amongst these grades, the high carbon variety has the drawback that though it is the least expensive, it raises the carbon content of the melt. This is undesirable, since all SS grades demand carbon contents less than 0.03%. As shown in Figure 4.1, chromium forms stable oxides. Hence, the removal of carbon from the bath by oxidation to CO is associated with the problem of simultaneous oxidation of chromium in molten steel. The higher the temperature, the greater is the tendency for preferential oxidation of carbon rather than chromium. From this point of view, higher bath temperatures are desirable; however, too high a temperature in the bath gives rise to other process problems.

The dilution of oxygen with argon lowers the partial pressure of CO, which helps in preferential removal of CO without oxidising bath chromium. Attempts were made to use this in the EAF, but the efforts did not succeed. Hence, as is the case with the production of plain carbon steels, the EAF is now basically a melting unit for stainless steel production as well. Decarburisation is carried out partially in the EAF, and the rest of the carbon is removed in a separate refining vessel. In this context, the development of the AOD process was a major breakthrough in stainless steelmaking.

AOD is the acronym for *Argon–Oxygen Decarburisation*. The process was patented by the Industrial Gases Division of the Union Carbide Corporation (now known as Praxair Inc.). In an AOD converter, argon is used to dilute the other gaseous species (O₂, CO, etc.). Hence, in some literature, it is designated as *Dilution Refining Process*. After AOD, some other dilution refining processes have been developed. Lowering of the partial pressures, such as the partial pressure of carbon monoxide, is achieved either by argon or by employing vacuum (Choulet and Masson, 1993; also Chapter 20 of this book). Figure 21.1 shows all the processes, including AOD, schematically. In Chapter 20 vacuum degassing and decarburisation processes have been discussed in connection with secondary steelmaking. Figures 20.11, 20.12 and 20.14 have presented some sketches of vacuum degassers.

The combination of EAF and AOD is sufficient for producing ordinary grades of stainless steels and this combination is referred to as a *Duplex Process*. Subsequent minor refining, temperature and composition adjustments, if required, can be undertaken in a ladle furnace. *Triplex refining*, where electric arc furnace melting and converter refining are followed by refining in a vacuum system, is often desirable when the final product requires very low carbon and nitrogen levels. Figure 21.2 depicts the triplex system, which makes the cycle time longer and adds to cost.

About 65–70% of the world's total production of stainless steel is in the austenitic variety, made by the duplex EAF–AOD route. If the use of AOD converters even in the triplex route is included, the share of AOD in world production would become as high as 75–80%.

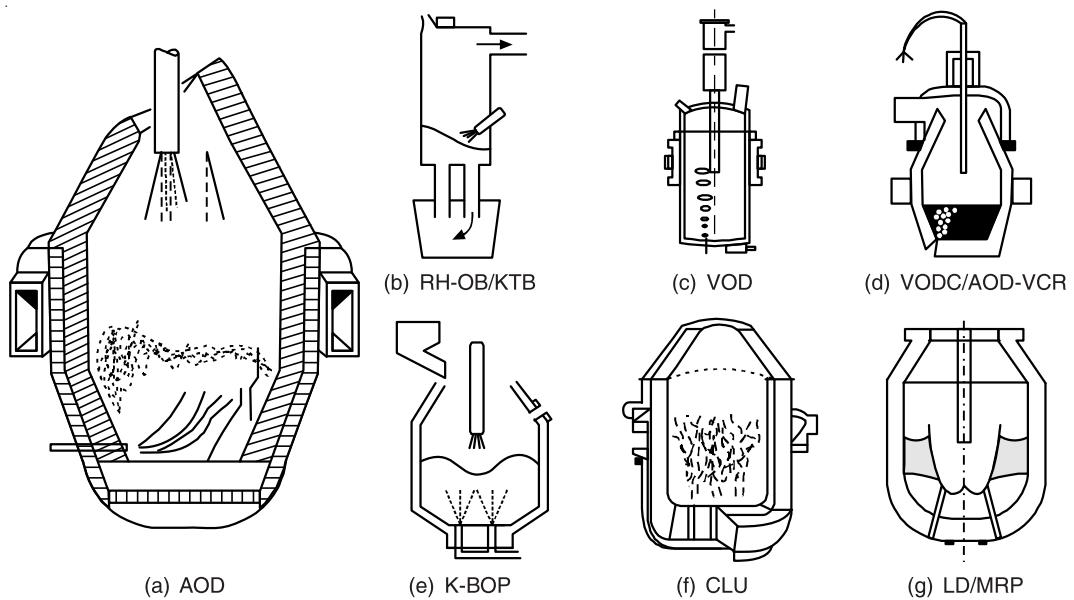


Figure 21.1 Processes for stainless steelmaking.

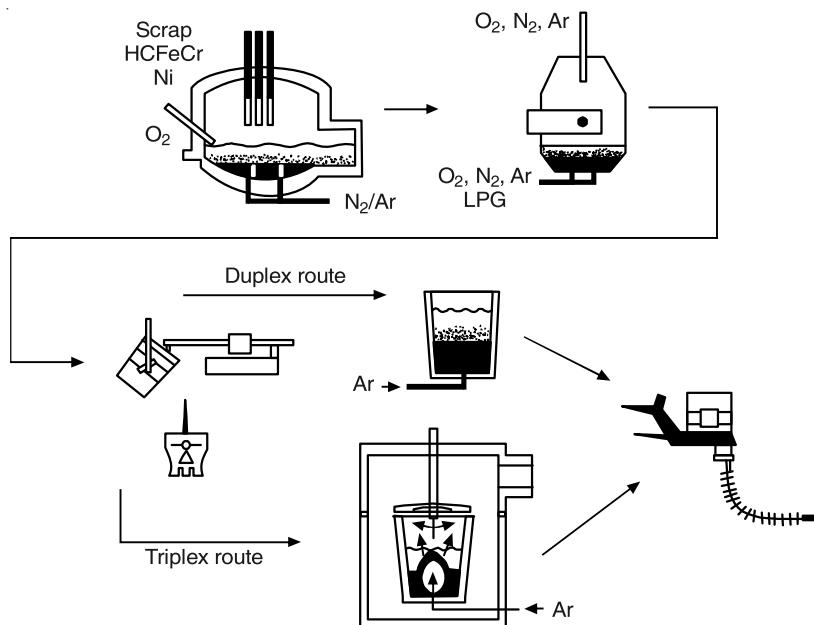


Figure 21.2 Illustration of duplex and triplex methods of stainless steelmaking.

In the situation where stainless steel scrap/ferrochrome is either very expensive or is not available, alternative process routes have been developed that use chromium ore and hot metal from blast furnaces or some other ironmaking unit. These processes typically consist of a smelting unit (often a converter) to reduce the ore, followed by decarburisation in another converter, sometimes followed by vacuum processing.

For further reading, the readers may consult (Hilty and Kaveney, 1985) and (Paul et al. 1999).

21.2 MELTING AND REFINING OF STAINLESS STEELS FOR SCRAP AND FERROALLOY-BASED PROCESSES

21.2.1 Melting

As already stated, the primary melting unit used for producing stainless steel is the electric arc furnace. Melting in induction furnaces is popular in the case of smaller scale operation and in foundries. Chapter 19 has dealt with EAF steelmaking for plain carbon steels including the recent developments, many of which have been employed for stainless steels as well. However, there are some salient differences.

1. Oxidation of chromium and transfer of the oxide to slag is not desirable, as it represents a loss of chromium. This sets a limit to the extent of oxygen blowing.
2. Carbon injection and foamy slag practices are rarely employed for SS. This is because the foam sustained by CO evolution is moderate and not vigorous during stainless steel melting.
3. Before tapping, ferrosilicon is often added to recover the oxidised chromium from the slag.

Stainless steel melting in some plants is also carried out in a converter. It requires the injection of carbon and oxygen and post-combustion of CO to CO₂ inside the converter to generate heat.

21.2.2 The AOD Converter Process

Figure 21.1(a) shows a sketch of an AOD converter. Molten steel containing most of the chromium and nickel needed to meet the final composition of SS steel, is tapped from the electric arc furnace into a transfer ladle. The AOD vessel is rotated into a horizontal position during charging of liquid steel, so that the side-mounted tuyeres are above the bath level. Then, the vessel is made vertical for gas blowing. Charging of solids during the blow, temperature measurement and sampling are done in a similar manner to that in BOF steelmaking.

In conventional AOD, no top blowing is involved. Only a mixture of argon and oxygen is blown through the immersed side tuyeres. However, the present AOD converters are mostly fitted with concurrent facilities for top blowing of either only oxygen, or oxygen plus inert gas mixtures using a supersonic lance as in BOF steelmaking. Initially, when the carbon content of the melt is high, blowing through the top lance is predominant though the gas mixture introduced

through the side tuyeres also contains a high percentage of oxygen. However, as decarburisation proceeds, oxygen blowing from the top is reduced in stages and argon blowing increased. As stated earlier, some stainless steel grades contain nitrogen as a part of the specifications, in which case, nitrogen is employed in place of argon in the final stages.

Use of a supersonic top lance as in the case of BOFs allows post-combustion of the evolved CO gas with consequent minimisation of toxic carbon monoxide in the exit gas as well as utilisation of the fuel value of CO to raise the bath temperature. Towards the end of the blow, when the carbon content is very low and is close to the final specification, only argon is blown to effect mixing and promote slag–metal reaction. At this stage, ferrosilicon and other additions are made. Silicon reduces chromium oxide from the slag. If extra-low sulphur is required, the first slag is removed and a fresh reducing slag is made along with argon stirring. The purpose of the other additions is to perform both alloying as well as cooling of the bath, since the bath temperature goes beyond 1700°C following the oxidation reactions.

21.2.3 Thermodynamics of Reactions in the AOD Process

Like iron, chromium exhibits two valencies, viz. Cr²⁺ and Cr³⁺, when it is oxidised. An issue on which controversies have persisted for long and continues even today is, whether chromium is present in slag as CrO, Cr₂O₃, or some other compound. From investigations carried out over the years, the picture that emerges is as follows. Like iron, chromium is capable of exhibiting a variable Cr²⁺/Cr³⁺ ratio in slag, depending on the oxygen potential and the basicity. In reducing slags or acid slags, CrO is the dominant oxide, whereas in oxidising or basic slags, Cr₂O₃ is the major species. During the oxidising period in a VOD or AOD, the slag may be assumed to be saturated with chromium oxide in view of the very small quantity of slag per tonne of metal. Based on evidence gathered, this oxide can be considered to be Cr₃O₄.

Hence, the reaction for the process is written as:



Since activity of Cr₃O₄ is 1 (since saturated), the equilibrium constant for the above reaction is:

$$K_1 = \frac{\{p_{CO}\}^4 \times [h_{Cr}]^3}{[h_C]^4} \quad (21.2)$$

Again, Eq. (21.2) may be rewritten as:

$$4 \log h_C = 3 \log h_{Cr} + 4 \log p_{CO} - \log K_1 \quad (21.3)$$

i.e. $4 \log W_C + 4 \log f_C = 3 \log W_{Cr} + 3 \log f_{Cr} + 4 \log p_{CO} - \log K_1 \quad (21.4)$

f_C and f_{Cr} are activity coefficients of carbon and chromium respectively in liquid iron for 1 wt.% standard state. They are functions of temperature and composition, while K_1 is a function of temperature. All these make the resulting equation somewhat cumbersome to use. It was simplified by Hilty and Kaveney (1985) as:

$$\log \left[\frac{W_{Cr}}{W_C} \right] = -\frac{13800}{T} + 8.76 - 0.925 p_{CO} \quad (21.5)$$

Figure 21.3 shows this relationship at one atmosphere pressure of CO (Hilty and Kaveney, 1985). It demonstrates that a very high temperature is required if it is required to obtain less than 0.04% C at above 15% Cr. Lowering of p_{CO} allows the same to be achieved at a much lower temperature. This is shown in Figure 21.4 (Hilty and Kaveney, 1985).

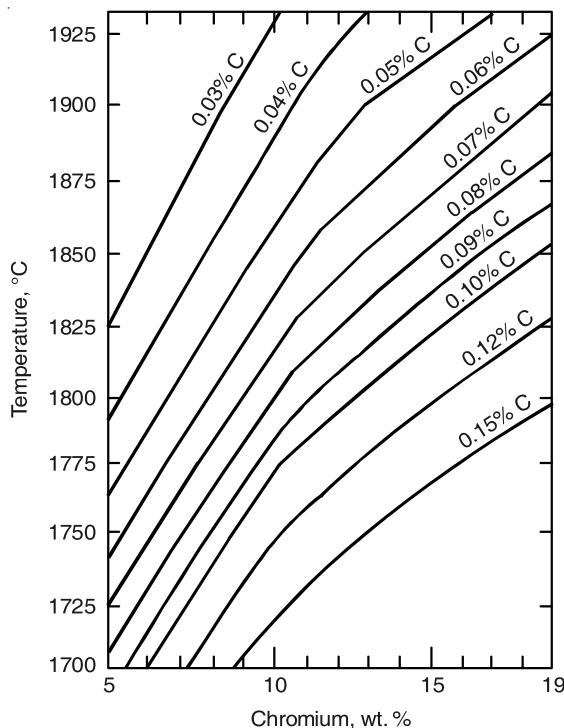
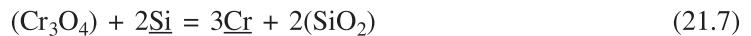


Figure 21.3 Chromium–carbon–temperature relationship in oxygen saturated steel melts.

Since nickel dissolved in liquid iron has a small but significant influence on the thermodynamic activities of carbon and oxygen, Eq. (21.5) was modified as:

$$\log \left[\frac{W_{Cr}}{W_C} \right] = -\frac{13800}{T + 4.21W_{Ni}} + 8.76 - 0.925p_{CO} \quad (21.6)$$

For the reduction of chromium oxide from slag by ferrosilicon during the last stages of VOD/AOD operation, Hilty et al. assumed the following reaction:



$$K_7 = \frac{[h_{Cr}]^3 (a_{SiO_2})^2}{[h_{Si}]^2 (a_{Cr_3O_4})} \quad (21.8)$$

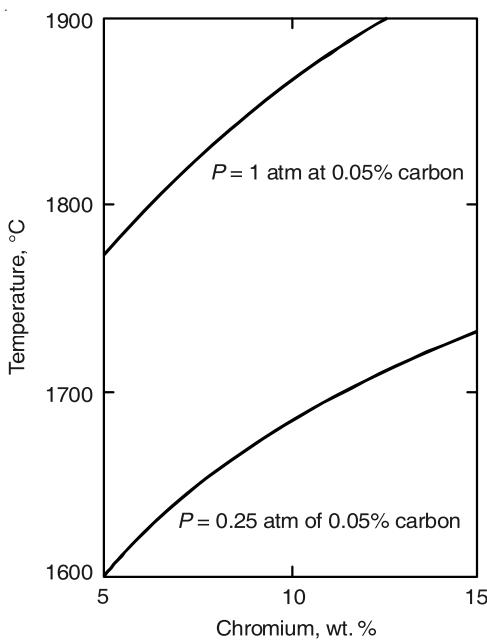


Figure 21.4 Influence of pressure and temperature on the retention of chromium by oxygen-saturated steel melts at 0.05% C.

Noting that a_{SiO_2} , $a_{\text{Cr}_3\text{O}_4}$ in slag are functions of slag basicity, an equilibrium relation was arrived at from Eq. (21.8). However, for practical purposes, statistically fitted empirical coefficients are recommended, such as:

$$\log (W_{\text{Cr}})_{\text{slag}} = 1.283 \log [W_{\text{Cr}}] - 0.748 \log [W_{\text{Si}}] - 1.709 \log V - 0.923 \quad (21.9)$$

where V = slag basicity = $(\text{CaO} + \text{MgO})/\text{SiO}_2$.

21.3 OTHER PROCESSES FOR STAINLESS STEELMAKING

Figures 21.1(b) to (f) schematically show the other types of reactors used; Table 21.1 provides a complete list. The principles and procedures followed in these processes are similar to those in AOD, except for minor details. As noted in Table 21.1, RH-OB/KTB, VOD and VODC/AOD-VCR processes are carried out under vacuum (Paul et al. 1999). Vacuum degassing and decarburisation have already been discussed in Chapter 20; therefore, detailed discussions are being omitted. Only some salient details are included below.

1. K-BOP was developed by Kawasaki Steel Corporation, Japan; K-OBM-S developed by Voest Alpine Industrie-Anlageneinbau (VAI), Austria, is a modified version of K-BOP.
2. CLU is the abbreviation of *Cruesot-Loire-Uddeholm*, jointly developed by Uddeholm, Belgium and Cruesot-Loire, France.
3. MRP is the abbreviation of *Metal Refining Process* developed by Mannesmann Demag, Germany. ASM stands for *Argon Secondary Melting* converter, also developed in Germany.