

Lecture 24: Principles of Deoxidation

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Introduction

Refining of hot metal to steel is done under oxidizing atmosphere. During refining oxygen dissolves in steel. Solubility of oxygen in steel is negligibly small. During solidification of molten steel, excess oxygen is rejected by the solidifying steel. This excess oxygen produces defects like blow holes and non-metallic oxide inclusion in solidified casting. Defects have considerable effect on mechanical properties of steel.

Therefore, it is necessary to remove oxygen from steel; removal of oxygen is called deoxidation.

Sources of oxygen in steel

- Rust on steel
- Oxygen blowing
- Steelmaking slag
- Atmospheric oxygen dissolved in steel during teeming
- Oxidizing refractories

At 1600°C solubility of oxygen in liquid steel is 0.23% which decreases to 0.003% in solid steel during solidification. According to the degree of deoxidation, carbon steels may be subdivided into three groups:

- i. Killed steel: Oxygen is removed completely. Solidification of such steels does not give gas porosity (blow holes).
- ii. Semi-killed steel: Incompletely deoxidized steels containing some amount of oxygen which forms CO during solidification.
- iii. Rimming steel: Partially deoxidized or non-deoxidized low carbon steels evolving sufficient CO during solidification. These steels have good surface finish.

Deoxidation of steel

Deoxidation can be carried out either by single element such as Si, Al, Mn etc or by mixture of elements such as Si + Mn, Ca – Si – Al etc. Deoxidation by single element is known as simple deoxidation,

whereas deoxidation by a mixture of elements is known as complex deoxidation. In both simple and complex deoxidation, oxide is formed; hence it is also termed precipitation deoxidation. Deoxidation is also carried out by carbon under vacuum; which is called vacuum deoxidation. Elements are added in the form of Ferro-alloys Fe – Si, Fe – Mn or Fe Si + Fe Mn etc.

Simple deoxidation can be represented by



If deoxidation product is pure then activity of $M_a O_b = 1$ and if elements are in dilute solution

$$[W_M]^a [W_O]^b = K_M. \quad (2)$$

Where K_M is deoxidation constant and equals to $\frac{1}{K_M^1}$ where K_M^1 is equilibrium constant.

$$\log K_M = -\frac{X}{T} + Y \quad (3)$$

Where X and Y are constants and T is temperature. Increase in T increases K_M . Using equations 2 and 3 one can calculate the variation of W_O with W_M when W_M is in small quantity. For larger W_M , interaction parameters need to be considered.

$$\log f_M = \sum_J e_M^J W_J \quad (4)$$

$$\log f_O = \sum_J e_O^J W_J \quad (5)$$

where J denotes all alloying elements. If steel contains C, and Mn.

$$\log f_O = e_O^O W_O + e_O^C W_C + e_O^{Mn} W_{Mn} \quad (6)$$

Where e is interaction parameter

All oxide products are definite compounds except compounds formed by Mn deoxidation. Here product is either solid MnO or liquid FeO. MnO .

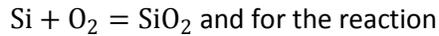
In complex deoxidation where a mixture of Si + Mn, Ca + Si, Ca + Si + Al is used, the following advantages are reported as compared with simple one:

- The dissolved oxygen is lower.
- Due to formation of liquid deoxidation product agglomeration of the product into large size can be obtained easily and can be floated easily.

According to equation 2

$$[W_O]^b = \frac{K_M}{[W_M]^a} \quad (7)$$

Equation 7 indicates that weight percent oxygen in steel depends on value of K_M for small concentration of deoxidizers. At 1600°C the value of K_M is 2.4×10^{-5} for the reaction



the value of $K_M = 3.32 \times 10^{-14}$. Similarly for the reaction $\text{Ca} + \text{O} = \text{CaO}$, $K_M = 9.84 \times 10^{-11}$. The value of K_M indicates the deoxidizing ability of an element. For the above reaction, calcium is the most efficient deoxidizer and Si is not so efficient as compared to calcium. Aluminum is also a strong deoxidizing element when compared with silicon.

Though calcium and aluminum are very efficient deoxidizers, but they oxidize very fast and moreover, their density is much lower than steel. Also Ca has a boiling point 1485°C which means calcium is gaseous phase at the steelmaking temperature. Suitable injection methods or addition methods are to be developed.

Kinetics of Deoxidation

Total oxygen in steel equals to dissolved oxygen + oxygen present in deoxidation products (SiO_2 , Al_2O_3 , MnO etc). Even if the dissolved oxygen is low, deoxidation products (also called inclusions) have to be removed, otherwise steel is not clean (clean steel refers to number and size of inclusions in steel). Kinetics of inclusion is concerned with deoxidation reaction and separation of deoxidation products as well. The deoxidation process consists of the following steps:

- Dissolution and homogenization of de oxidizer. Mechanism of dissolution depends on melting point. Ferro alloys melt at around 1500°C. Aluminium is expected to melt faster due to its much lower point. Intensity of agitation will govern the homogenization of deoxidizer in steel melt for faster kinetics of reaction between oxygen and deoxidizer.
- Nucleation of solid product becomes easier if interface is present. Deoxidation by Al produces solid Al_2O_3 and as such Al_2O_3 /steel interface is useful for nucleation.
- Growth of the de oxidation product: It depends on the state of the product. A liquid product can coalesce easily as compared with the solid product. Deoxidation with single elements like Al, Si etc. produce solid deoxidation product at the steelmaking temperature. Deoxidation with ferro silicon+ ferro manganese produces liquid deoxidation product. Boron, titanium zirconium are also quite effective deoxidizers. Manganese and silicon are used in the ratio 7:1 to 4:1 in order to obtain a thin liquid slag.
- Removal of deoxidation product: Removal of de oxidation product is equally important. It is achieved by floatation and absorption into a slag. Following steps are important for removal of de oxidation products from steel:
 - i. Growth of de oxidation product
 - ii. Movement through molten steel to surface

iii. Absorption of inclusion by a suitable designed synthetic slag.

Floation of an oxide product depends among physical properties of steel, on the size of the product. The rate of rise of a spherical particle in a quiet fluid or in a fluid of laminar flow (i.e. at very low Reynold's number) can be described at steady state by Stoke's law:

$$V_t = \frac{gd^2\Delta\rho}{18\eta} \quad (8)$$

V_t = terminal velocity (m/s) of the inclusion, g is acceleration due to gravity (m/s^2), $\Delta\rho$ = deifference in density of steel and deoxidation product and η is viscosity of steel (kg/m. s).

Deoxidation products are lighter than steel; hence they move up. According to equation 8 the rising velocity is proportional to square of the size of the deoxidation product. Larger sizes move faster. Moreover different sizes of de oxidation product will move with different velocities. During their movement, they may collide with one another. Stirring of melt may help floating of de oxidation products.

Degree of stirring in the melt is important. Vigorous stirring may not be of much help since deoxidation product may be circulated in the liquid.

For the removal of deoxidation product, equally important is the design of synthetic slag to absorb the deoxidation product.

Deoxidation practice

Deoxidation can be carried out during tapping, in ladles runners and even in moulds. Bath stirring is important. During tapping, bath is stirred due to potential energy but this subsides towards the end. When deoxidation is carried out in ladle, it is called ladle deoxidation in industrial practice. Depending on the extent of deoxidation, killed, semi killed and rimming steels are produced. For carbon content less than 0.15% and enough oxygen in steel, rimming steel can be produced.

Alloy steels are fully killed to obtain maximum recovery of alloying additions.

Illustration

Let us take an example of deoxidation of steel with ferromanganese. Manganese is a weak deoxidizer. We intend to reduce the dissolved oxygen in steel from 0.045 wt.% to 0.018 wt.%. How much manganese would be required?

Consider the reaction

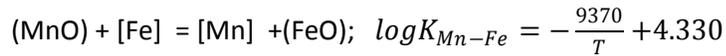
$$(MnO) = [Mn] + [O]; \log K_{Mn} = -\frac{11070}{T} + 4.526$$

We can write $\frac{W_{Mn}}{X_{MnO}} = \frac{K_{Mn}}{W_O}$, we have assumed $h_{Mn} = W_{Mn}$ and $h_O = W_O$, where W_O is weight percent

Substituting the value of $K_{Mn} = 0.0413$ at 1600°C and $W_O = 0.018$ we get

$$\frac{W_{Mn}}{X_{MnO}} = 2.29$$

For the deoxidation with manganese, the following reaction must also be considered



By writing equilibrium constant and using the value of $\frac{W_{Mn}}{X_{MnO}} = 2.29$ we can find $X_{\text{FeO}} \approx 0.9$ and $W_{Mn} = 2.061$ wt. percent.

Total manganese required would be equal to manganese required to remove (0.045% – 0.018%) oxygen + Manganese required to raise the content of Mn from 0.1% to 2.061%

Calculation gives 20.53Kg Mn/ton steel. If the manganese content of ferromanganese is 60%, ferromanganese would be 34 kg/ton of steel

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