# Lecture 29 inclusion Engineering

Preamble

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Inclusion engineering by calcium treatment

Oxide shape control

Sulphide shape control

Effect of rare earth elements

Key words: Inclusion engineering, clean steel, steelmaking

## Preamble

Inclusions engineering technology is based on the design of inclusions so as to alleviate their harmful effects on the product properties.

Inclusion engineering does not refer to removal of inclusions but it refers to modify them either in terms of chemical composition or shape so that harmful effects of the inclusions can be converted to improve the steel properties.

Inclusion engineering also involves distribution of inclusion uniformly in the matrix. So that composite properties can be generated in the product.

In some cases, deliberate attempts are made to form very fine inclusions (e.g. nitrides, and carbonitrides inclusions in hardening steel). Such inclusion can form by reaction between Ti, W,Al with O, N, S or C.

Macro-size inclusions must be removed. In all other cases, depending on applications, inclusion can be modified to minimize their harmful effects.

## Requirements for inclusion engineering

One of the main requirements is to find an element which should be added to modify the inclusion. Element should meet the following

- It should have high chemical affinity for the inclusion

- It should be able to modify the composition so that it becomes liquid.

- It should also be able to modify the shape i.e. sharp edges ands corner of inclusions to spherical.

**What types of inclusions need to be modified?**

Mainly $Al_2O_3$ and $MnS$ inclusions are modified. $Al_2O_3$ inclusions are brittle and breaks on deformation. Similarly $MnS$ inclusion in steel on deformation becomes stringer type.

**Inclusion engineering**

In aluminum killed steels, alumina inclusions are formed. Alumina inclusions are solid at steelmaking temperature. During continuous casting, alumina inclusions clog the nozzle and consequently steel flow rate to the mold is affected.   Calcium is used widely to modify inclusions in continuous casting of steel. The solubility of calcium in steel is 320 ppm. The density of calcium is 1.55 $^g/_{cm^3}$  and is in vapour form at steelmaking temperature$(1600°C)$. Therefore suitable injection methods for calcium have to be developed.

One method is to inject calcium deep into the molten bath such that the ferrostatic pressure overcomes vapor pressure of calcium. In another method wire containing calcium components are injected at speeds of 80-300 m/min. Typically Ca-Si powder in which calcium content is 20-30% is used in the wire. Wire containing Ca-Si powder is injected deep into bath to avoid **a)** oxidation of Ca and **b)** to keep calcium in the liquid form.

Addition of calcium in steel containing oxygen and sulphur can form two phases: oxide and sulphide. Oxide phase consists of the compounds in $CaO - Al_2O_3$ system. The different oxide compounds have different melting temperature as shown in the table.

| Compound | Melting point (K) | Ca/Al |
|---|---|---|
| 3 CaO. $Al_2$ $O_3$ | 1800 | 2.22 |
| 12 CaO.7 $Al_2$ $O_3$ | 1673 | 1.27 |
| CaO. $Al_2$ $O_3$ | 1868 | 0.74 |
| CaO. 2 $Al_2$ $O_3$ | 2000 | 0.37 |

It may be noted that in$12$ $CaO.Al_2O_3$has low melting point and it will remain in the liquid  at steelmaking temperature. The table also shows Ca/Al ratio in various $CaO.Al_2O_3$  compounds. The Ca/Al ratio is 1.27 in$12$ $CaO.7$ $Al_2O_3$  compounds. This suggests that calcium/aluminum ratio has to be adjusted at 1.27 (theoretically) in order to obtain liquid product.

 The sulphide phase consists of CaS and MnS. The melting point of CaS is $2000°C$  and that of MnS $1610°C$. $CaO.Al_2O_3$ melt has some solubility for CaS.

**Oxide shape control**

 It consists of modifying $Al_2O_3$  inclusions. $Al_2O_3$ is solid at steelmaking temperature and is brittle in nature. On rolling, alumina inclusions break up which is a serious surface defect. The alumina may accumulate in the continuous casting nozzle causing clogging of the nozzle.

For a normal aluminum killed steel calcium will first modify the oxide inclusions. Thermodynamically it is easier to form $CaO.\,2\,Al_2O_3$ type of inclusions which will be converted to $CaO.\,Al_2O_3$ and finally liquid calcium aluminate rich is$CaO$. The calcium will then desulphurize steel to very low levels.

Thus it is possible that calcium will react with sulphur to form CaS before there is oxide shape modification. The sulphur level where CaS is more stable will depend on Al content. It must also be noted that $12\,CaO.\,7\,Al_2O_3$ is liquid product at steelmaking temperature. Thus it is important to control the concentration of Al, S and Ca in molten steel for engineering of oxide inclusions.

**Sulphide shape control**

MnS has a low melting point and elongate in the direction of rolling and becomes stringer type inclusions. These inclusions greatly reduce the transverse mechanical properties of steel. MnS also causes steel to be more susceptible to hydrogen induced cracking. Stringer type inclusions should be modified if not eliminated.

Formation of MnS requires thermodynamically that the solubility product

$$[\%Mn] \times [\%S] > 2$$

at the solidification temperature. During solidification, Mn and S are rejected from the solid steel causing an increase in their concentration in the remaining liquid. The Mn and S enriches in the interdendritic region and MnS forms during the end of solidification.

For sulphide shape control, it is necessary to desulphurize steel to very low value say $0.006\%$. Addition of calcium to aluminum killed steel will first form calcium aluminate inclusion. If calcium aluminate inclusion has excess $CaO$ content, it has high sulphide capacity as well. This will result in precipitation of CaS which forms a duplex inclusion in which a $CaS - MnS$ ring surrounds calcium aluminate core. This type of inclusion is spherical and does not elongate.

**Effect of rare earth elements**

When rare earths (elements) like cerium, lanthanides are added to steel they can react to form an oxide, sulphide or oxysulphides:

$$2\,Ce + 3O = Ce_2O_3$$
$$Ce + S = CeS$$
$$2Ce + 2O + S = Ce_2O_2S$$
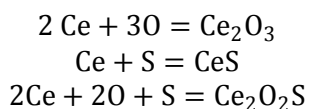
Correct addition of rare earth elements like cerium forms oxysulphide inclusion.

It must be noted that rare earths have high atomic weights, and their oxides, sulphides and oxysulphides have high density 5 to 6 $g/cm^3$ as compared with other oxides. These inclusions do not float easily. Rare earths are strong deoxidizers and desulphrizers as well.

As an example of inclusion engineering, oxide inclusions have been designed to make them useful to increase the machine tool life. Subramanian et al has designed tool steel to be self lubricating by

modifying the rheology of oxide inclusions. Glassy inclusions are designed to soften at the tool/chip interface temperature so that a viscous layer of glass can lubricate the tool-chip interface. The interested reader may go through the references.

References:

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