Lecture 4: Slag in steelmaking

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Keywords: Steelmaking, synthetic slag, Electric steelmaking, BOF steelmaking

Preamble

Slag plays a very important role in steelmaking to the extent that it is said that "make a slag and slag makes steel". Slag is a generic name and in steelmaking it is mostly a solution of oxides and sulphides in the molten state and the multi-crystalline phases in the solid state.

Slag is a separate phase because

- It is lighter than molten steel and
- It is immiscible in steel

Slag is formed during refining of hot metal in which Si oxidizes to SiO_2, Mn to MnO, Fe to FeO, and P to P_2O_5, and addition of oxides such as CaO, MgO, iron oxide, and others. The addition of oxides is done to obtain desired physico-chemical properties of slag like melting point, basicity, viscosity etc. All these oxides float on the surface of the molten steel. Synthetic slag is also used to absorb inclusions to produce clean steel for certain applications.

The role of slag in steelmaking:

- It acts as a sink for impurities during refining of steel
- It controls oxidizing and reducing potential during refining through FeO content. Higher FeO makes the slag oxidizing and lower FeO reducing
- It prevents passage of nitrogen and hydrogen from atmosphere to the molten steel
- It absorbs oxide/sulphide inclusions

- It acts as a thermal barrier to prevent heat transfer from molten steel to the surrounding.

- It protects steel against re-oxidation

- It emulsifies hot metal and promotes carbon oxidation.

- In electric steelmaking slag prevents the radiation of heat of arc to the wails of the furnace and roof

The above functions require that slag should possess certain physical (density, melting point, viscosity) and chemical properties (basicity, oxidation potential). Both physical and chemical properties are controlled by composition and structure of slag. In steelmaking slag is predominantly a mixture of oxides with small amounts of sulphides and phosphides. The oxides are either acidic or basic in nature. We will first consider the structure of pure oxides and then we discuss what happens on addition of one type of oxide to the other.

Structure of pure oxides

In pure oxides

- Metallic cations are surrounded by oxygen ions in a three dimensional crystalline network

- Each cation is surrounded by the maximum number of anions in a closed packed structure, and this number is called coordination number

- Cations of basic oxides such as CaO, MgO, FeO ($Ca^{2+}, Mg^{2+}, Fe^{2+}$) etc. have radii smaller than that of cations of SiO_2, Al_2O_3

- Structure of an oxide depends on the ratio of radii of cations/anions as shown in the following table

Structure	CN	Cation/anion	Examples
Cubic	8	1 – 0.732	
Octahedral	6	0.732 – 0.414	CaO, MgO, MnO, FeO etc.
Tetrahedral	4	0.414 – 0.225	SiO_2, P_2O_5
Triangular	3	0.225 – 0.133	

CN= Coordination number

As can be seen in the table the basic oxides have octahedral and acidic oxides tetrahedral structure.

Structure of pure silica

In silica, each atom of silicon is bonded with four oxygen atoms and each atom of oxygen is bonded with two silicon atoms. The elemental tetrahedral of silica are joined at the vertices to give the hexagonal network in three dimensions. The structure of pure solid and molten silica is shown in the figure

Figure 3.1: Structure of silica (a) solid and (b) molten

As seen in the figure 3.1a, each tetrahedron is joined at the vertex so as to obtain the three dimensional hexagonal network. During melting the crystalline network of silica is broken by thermal agitation as shown on figure 3.1b. Only at very high temperatures, molten silica consists of equal number of SiO_4^{4-} and Si^{4+} ions.

Network former and breaker oxides

It must also be understood that the bonding between cations and anions in acidic oxides like SiO_2 and P_2O_5 is strong, and these simple ions group to form complex ions as $(SiO_4)^{4-}$ and $(PO_4)^{3-}$. In slags, these tend to form hexagonal network. These oxides are, therefore, called network formers or acids. These acidic oxides can accept one or several oxygen ions.

Basic oxides like CaO, MgO, Na_2O, FeO dissociate and form simple ions like Ca^{2+} and O^{2-}. All basic oxides are donors of oxygen ions. These oxides are called network breakers, since they destroy the hexagonal network of silica by reacting with it.

Structure of slag

Most slags are silicates. Pure silica has very high viscosity at the melting point. Addition of basic oxides decreases the viscosity by breaking the hexagonal network of silica. Consider the addition of CaO to molten silica. Calcium oxide dissociates to

$$CaO = Ca^{2+} + O^{2-}$$
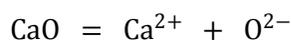
Each mole of CaO introduces one mole of oxygen ions in the hexagonal network of silica and can break two vertices of the hexagonal structure of silica. By adding 2 moles of O^{2-} for every mole of silica all the four vertices are broken and we simply have Ca^{2+} and SiO^{4-} as shown below
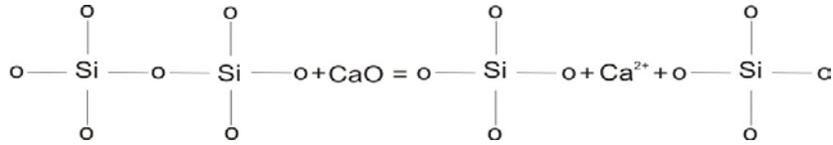
Note that Ca^{2+} can combine with two tetrahedrons

The reaction between alkaline base oxides, e.g. Na_2O and SiO_2 is as follows:

$$Na_2O \;+\; 2Na^+ \;+\; O^{2-} \text{ and}$$
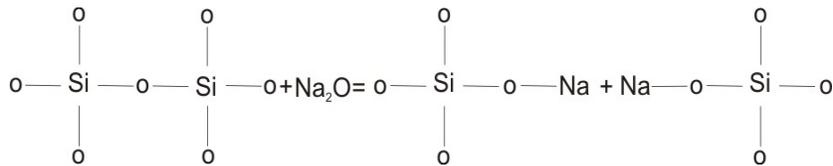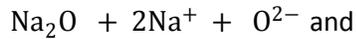
Since Na has one charge, each tetrahedron of silica will have Na ion attached to oxygen ion. As a result one should expect more decrease in viscosity of silica on addition of alkaline base oxides as compared with basic oxides.

The number of vertices destroyed depends on the fraction of basic oxide, i.e. the ratio of O/Si as shown in the table

O:Si	Formula	Structure	Equivalent silicate ions
2:1	SiO_2	All corners of tetrahedron are shared	$(Si_6O_{15})6^-$ or $(Si_8O_{20})8^-$
5:2	$MO.2SiO_2$	One broken link per tetrahedron	$(Si_3O_9)6^-$ or $(Si_4O_{12})8^-$
3:2	$MO.SiO_2$	Two broken link per tetrahedron	$(Si_3O_9)6^-$
7:2	$3MO.2SiO_2$	Three broken link per tetrahedron	$(Si_2O_7)6^-$
4:1	$2MO.SiO_2$	All link are broken	$(SiO_4)^{4-}$

All the four vertices will be broken when 2 moles of CaO are added for each mole of silica. The resulting slag would consist of Ca^{2+} and SiO_4^{4-} ions

References

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