Lecture 14: Refractory Materials

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Key words: Refractory, steelmaking, furnaces, smelting, blast furnace, soaking pits, annealing furnaces

What is a refractory and why is it required?

Refractory is a material which can withstand high temperature and does not fuse. Examples are: fireclay, alumina, magnesite, chrome magnesite, dolomite etc.

Refractory materials are produced to meet the diversified Requirements of high temperature processes carried out in metal extraction, cement, glassmaking, manufacturing, ceramic etc. industries. The refractory is required

- To allow thermal energy dependent conversions of reactants into products because metallic vessels are neither suitable nor economical
- Source of energy in high temperature processing is mostly fossil fuels either directly or indirectly i.e. electricity derived from fossil fuels. Thus refractory should minimize heat losses to conserve energy resources.
- Because the reaction chamber is constructed of refractory material, refractory is required to sustain the physico-chemical attack of different phases at different intervals of time doing processing.

What are the phases?

The following phases are important in high temperature processing to design the refractory for a given requirement

a) Slag: It is a mixture mostly molten oxides and sulphides, in some processes phosphate is also a constituent of slag. Oxides are either acidic such as silica, fireclay or basic like MgO, MgO-C, alumina, FeO.

Among sulphides CaS, MnS, FeS, PbS etc, are prominent phases. The slag is molten and its temperature in different processing lay within the range 1200-1600°C.
b) Liquid metal

In metal extraction from ores, metal is extracted in the liquid stage. Composition of metal, and its temperature are important. For example in iron and steel industry, hot metal is a mixture of iron, carbon, silicon, manganese and phosphorus. The temperature varies in between 1300 °C to 1600°C. In copper-making the temperatures are within the range 1100-1200°C. Molten aluminum is produced at700-750°C, and likewise other non ferrous metals.

c) Matte: it is a high temperatures molten phase and consists of a mixture of molten sulphides like Cu₂S, FeS, Ni₃S₂ etc. The temperatures vary within the range 1100°C to 1250°C.

d) Gases: Several different types of gases like CO, CO₂, N₂ H₂O (vapor), argon, O₂ are used at high temperatures in several unit processes like roasting, calcination, smelting, refining, converting etc. The temperatures may vary in between 600°C to1500°C. The gases like CO₂, H₂O, and O₂ are oxidizing, whereas the gases like CO, and H₂ are reducing. N₂ and argon are inert.

e) Speisses are molten solutions of arsenides, or arsenides and antimonides when the materials being treated contain large quantities of As and Sb.

f) Drosses are heterogeneous products skimmed or driven form the surface of molten metal during refining. They are mixtures of precipitated solid and liquid compounds with substantial proportion of mechanically trapped molten metal.

**Properties required in a refractory**

The diversified applications of refractory materials in several different types of industries require diversified properties to meet the physico-chemical and thermal requirements of different phases. In some industrial units more than one phase are present e.g. in steel-making vessels slag /metal /gases are simultaneously present in the vessel at high temperatures. In the heat treating furnaces solid/reducing or oxidizing gases are simultaneously present. Below are briefly described the properties of the refractory materials:

**Refractoriness**

Refractoriness is a property at which a refractory will deform under it own load. The refractoriness is indicated by PCE (Pyrometric cone equivalent). It should be higher than the application temperatures.

Refractoriness decreases when refractory is under load. Therefore more important is refractoriness under load (RUL) rather than refractoriness.

**Porosity and Slag permeability**

Porosity affects chemical attack by molten slag, metal and gases. Decrease in porosity increases strength and thermal Conductivity.
**Strength**

It is the resistance of the refractory to compressive loads, tension and shear stresses.

In taller furnaces, the refractory has to support a heavy load; hence strength under the combined effect of temperature and load, i.e. refactoriness under load is important.

**Specific gravity**

Specific gravity of the refractory is important to consider the weight of a brick. Cost of bricks of higher specific gravity is more that of lower specific gravity. But strength of bricks of higher specific gravity is greater than one with lower specific gravity.

**Spalling**

Spalling relates to fracture of refractory brick which may occur due to the

- Temperature gradient caused by sudden heating or cooling
- Compression in a structure of refactoriness due to expansion
- Variation in coefficient of thermal expansion between the surface layer and the body of the brick due to slag penetration or to a structural change.

On sudden heating

\[
\text{Spalling tendency} \propto \frac{\text{coeff. of thermal expansion}}{\text{max}^m \text{shearing strain} \sqrt{\text{thermal diffusivity}}}
\]

On sudden cooling

\[
\text{Spalling tendency} \propto \frac{\text{coeff. of thermal expansion}}{\text{max}^m \text{tensile strength} \sqrt{\text{thermal diffusivity}}}
\]

**Permanent Linear change (PLC) on reheating**

In materials certain permanent changes occur during heating and these changes may be due to

- Change in the allotropic form
- Chemical reaction
- Liquid phase formative
- Sintering reactions

\[
\text{PLC(%)linear} = \frac{\text{Increase in length}}{\text{original length}} \times 100
\]

\[
\text{PLC(%)volume} = \frac{\text{Increase in volume}}{\text{original volume}} \times 100
\]

These changes determine the volume stability and expansion and shrinkage of the refractory at high temperatures.

**Thermal conductivity**
Thermal conductivity of the bricks determine heat losses. Increase in porosity decreases thermal conductivity but at the same time decreases strength also.

**Bulk density:**

Decrease in bulk density increases volume stability, heat capacity.

**Selection of refractory**

Selection of a refractory is complicated. Among physic-chemical –thermal properties, cost is the most important. Broadly speaking selection may depend on

1) **Furnace Design**

   a) *How the furnace is to be heated;* whether directly or indirectly. In indirect heating e.g coke oven, Pidgeon’s process for Mg production, Kroll’s process (production of Ti by reduction of TiCl₂ with Mg), walls of the furnace are heated and heat is transferred from the walls to the charge. Among other properties, thermal conductivity of the refractory is important. Whereas in direct heating fuel and air mixture is supplied to the furnace and here wall of the refractory facing the reaction chamber must have high refractoryness besides other properties.

   b) *Condition of heating:*

   There are furnaces which operate continuously and others batchwise. For example coke oven is kept continuously at high temperature for months but a cupola operates intermittently.

   c) **Loading**

   Loading and unloading required/ unit time

2) **Operating Factor**

   a. *Chemistry of phases:*

   The different phases are present at different intervals of time during processing. The combination of different phases is shown in the figure given below:

   *Figure........................*

   The refractory facing these phases needs careful selection.

   b. *Temperature:*

   High temperatures are involved in industrial furnace. The reaction chamber temperatures may vary from 1200-1600°C in liquid stale processing and 700-1200°C in various solid stale processing operations.

   *C. Abrasion due to movement*
Molten metal and slag are turbulent in nature. Gases are flowing at high speeds inside the reactors. The refractory chamber should be able to withstand the erosion and corrosion caused by the movement of the phases.

\textit{d) Lining life}

Lining life, i.e. time for complete relining of the furnace is an important consideration and depends on several factors like, maintenance and repair technologies, condition of the phases, temperature, quality of the refractory etc.

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