

LECTURE 9 Refractory Materials

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Role of refractory

Refractory materials have a crucial impact on the cost and quality of steel products. The diversification on steel products and their cleanliness requirement in recent years have increased the demand for high quality refractory. Steelmaking requires high temperatures of the order of 1600 degree centigrade. In addition steelmaking handles high temperature phases like molten steel, slag and hot gases. These phases are chemically reactive; refractory materials are required to produce steels. High quality refractory at a cheaper cost is the main requirement because cost of refractory adds into the cost of product.

What is a refractory?

Refractories are inorganic nonmetallic material which can withstand high temperature without undergoing physico – chemical changes while remaining in contact with molten slag, metal and gases. It is necessary to produce range of refractory materials with different properties to meet range of processing conditions.

The refractory range incorporates fired, chemically and carbon bonded materials that are made in different combinations and shapes for diversified applications.

Why required?

- To minimize heat losses from the reaction chamber

- To allow thermal energy dependent conversion of chemically reactive reactants into products because metallic vessels are not suitable.

In steelmaking, the physico- chemical properties of the following phases are important:

Slag: Mixture of acidic and basic inorganic oxides like SiO_2 , P_2O_5 , CaO , MgO , FeO , etc.; temperature varies in between 1400°C to 1600°C .

Molten steel: Iron containing carbon, silicon, manganese, phosphorous, tramp elements, non metallic inclusions, dissolved gases like nitrogen, oxygen and hydrogen and different alloying elements like Cr, Ni, Nb, Mo, W, Mo etc.; temperature 1600°C

Gases: CO , CO_2 , N_2 , Ar containing solid particles of Fe_2O_3 , Fe_3O_4 etc.; temperature 1300°C to 1600°C .

The above phases are continuously and constantly in contact with each other and are in turbulent motion.

Refractory requirements:

The refractory materials should be able to withstand

- High temperature
- Sudden changes of temperature
- Load at service conditions
- Chemical and abrasive action of phases

The refractory material should not contaminate the material with which it is in contact.

Melting point of some pure compounds used to Manufacture refractory

Compounds	Melting point ($^\circ\text{C}$)
MgO (pure sintered)	2800
CaO(limit)	2571
SiC pure	2248
MgO (90-95%)	2193
Cr_2O_3	2138
Al_2O_3 (pure sintered)	2050
Fireclay	1871
SiO_2	1715

Kaolin ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$)	1816
Chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$)	2182

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 its 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. refractoriness 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 than 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 following reasons:

- A temperature gradient in the brick which is caused by sudden heating or cooling.

- Compression in a structure of refractory due to expansion
- Variation in coefficient of thermal expansion between the surface layer and the body of the brick
- Variation in coefficient of thermal expansion between the surface layer and the body of the brick is due to slag penetration or due to 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

$$\text{PLC}(\%)_{\text{linear}} = \frac{\text{Increase /decrease in length}}{\text{original length}} \times 100$$

$$\text{PLC}(\%)_{\text{volume}} = \frac{\text{Increase /decrease in volume}}{\text{original volume}} \times 100$$

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

Thermal conductivity

Thermal conductivity of the bricks determines 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.

Types of refractory materials

This can be discussed in several ways, for example chemical composition of refractory or use of refractory or method of manufacture or in terms of physical shape. Below is given type of refractory depending on its chemical composition and physical shape.

A) Chemical composition

Refractories are composed of either single or multi-component inorganic compounds with non metallic elements.

Acid refractory

The main raw materials used are SiO_2 , ZrO_2 and aluminosilicate. They are used where slag and atmosphere are acidic. They cannot be used under basic conditions. Typical refractories are fireclay, quartz and silica.

Basic refractory

Raw materials used are CaO , MgO , dolomite and chrome-magnesite. Basic refractories are produced from a composition of dead burnt magnesite, dolomite, chrome ore.

- a) Magnesite: Chrome combinations have good resistance to chemical action of basic slag and mechanical strength and volume stability at high temperatures.
- b) Magnesite: Carbon refractory with varying amount of carbon has excellent resistance to chemical attack by steelmaking slags.
- c) Chromite- Magnesite refractory: used in inner lining of BOF and side walls of soaking pits. (basic refractory)
- d) Magnesite: Basic refractory in nature. Magnesite bricks cannot resist thermal shock, lose strength at high temperature and are not resistant to abrasion.

Neutral refractory

Neutral refractory is chemically stable to both acids and bases. They are manufactured from Al_2O_3 , Cr_2O_3 and carbon.

For details readers may see the references given at the end of lecture 10.

B) Physical form

Broadly speaking refractory materials are either bricks or monolithic.

Shaped refractories are in the form of bricks of some standard dimensions. These refractories are machine pressed and have uniform properties. Special shapes with required dimensions are hand molded and are used for particular kilns and furnaces. Different types are:

- i. Ramming refractory material is in loose dry form with graded particle size. They are mixed with water for use. Wet ramming masses are used immediately on opening.

- ii. Castables refractory materials contain binder such as aluminate cement which imparts hydraulic setting properties when mixed with water. These materials are installed by casting and are also known as refractory concretes.
- iii. Mortars are finely ground refractory materials, which become plastic when mixed with water. These are used to fill the gap created by a deformed shell, and to make wall gas tight to prevent slag penetration. Bricks are joined with mortars to provide a structure.
- iv. Plastic refractories are packed in moisture proof packing and pickings are opened at the time of use. Plastic refractories have high resistance to corrosion.

Monolithic refractories

Monolithic refractories are replacing conventional brick refractories in steelmaking and other metal extraction industries. Monolithic refractories are loose materials which can be used to form joint free lining. The main advantages of monolithic linings are

- Greater volume stability
- Better spalling tendency
- Elimination of joint compared with brick lining
- Can be installed in hot standby mode
- Transportation is easier

Monolithic refractories can be installed by casting, spraying etc.

Ramming masses are used mostly in cold condition so that desired shapes can be obtained with accuracy.

Insulating materials

The role of insulating materials is to minimize heat losses from the high temperature reactors. These materials have low thermal conductivity while their heat capacity depends on the bulk density and specific heat. Insulating materials are porous in structure; excessive heat affects all insulating materials. Choice of insulating materials would depend upon its effectiveness to resist heat conductivity and upon temperature. High alumina with thermal conductivity $0.028 \frac{\text{kcal}}{\text{m}^\circ\text{C}}$, and silica with thermal conductivity $0.04 \frac{\text{kcal}}{\text{m}^\circ\text{C}}$ etc are amongst others, used as insulating materials.

Ceramic fibres are important insulating materials and are produced from molten silica, titania, Zirconia etc in the form of wool, short fibres and long fibres. They have excellent insulation efficiency. They are long weight.

References:

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