

Refractories

Refractories are inorganic nonmetallic material which can withstand high temperature without undergoing physical or 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.

Refractories are material having high melting points, with properties that make them suitable to act as heat-resisting barriers between high and low temperature zones.

ASTM C71 defines refractories as "non-metallic materials having those chemical and physical properties that make them applicable for structures or as components of systems that are exposed to environments above 1000 °F (538 °C)".

Refractories are useful in constructing application-specific high temperature areas/surfaces, particularly in furnaces or boilers, as they minimize heat losses through structure.

Depending on the operating environment, they need to be resistant to thermal shock, be chemically inert, and/or have specific ranges of thermal conductivity and of the coefficient of thermal expansion.

Alumina, silica and magnesia are the most important materials used in the manufacturing of refractories. Another oxide usually found in refractories is the oxide of calcium (lime). Fire clays are also widely used in the manufacture of refractories.

Refractories must be chosen according to the conditions they will face. Some applications require special refractory materials. Zirconia is used when the material must withstand extremely high temperatures. Silicon carbide and carbon (graphite) are two other refractory materials used in some very severe temperature conditions, but they cannot be used in contact with oxygen, as they will oxidize and burn. The principal raw materials used in the production of refractories are: the oxides of silicon, aluminum, magnesium, calcium and zirconium and some non-oxide refractories like carbides, nitrides, borides, silicates and graphite.

Basic functions Refractories:

1. They act as a thermal barrier between a hot medium (e.g., flue gases, liquid metal, molten slags, and molten salts) and the wall of the containing vessel.
2. They insure a strong physical protection, preventing the erosion of walls by the circulating hot medium.
3. They represent a chemical protective barrier against corrosion.
4. They act as thermal insulation, insuring heat retention.

Uses of Refractories

1. Refractories are used by the metallurgy industry in the internal linings of furnaces, kilns, reactors and other vessels for holding and transporting metal and slag.
2. In non-metallurgical industries, the refractories are mostly installed on fired heaters, hydrogen reformers, ammonia primary and secondary reformers, cracking furnaces, utility boilers, catalytic cracking units, coke calciner, sulfur furnaces, air heaters, ducting, stacks, etc.
3. Majority of these listed equipment operate under high pressure, and operating temperature can vary from very low to very high (approximately 900°F to 2900°F).
4. The refractory materials are therefore needed to withstand temperatures over and above these temperatures.
5. Due to the extremely high melting point of common metals like iron, nickel and copper, metallurgists have to raise furnace temperatures to over 2800°F.

Characteristics or requisites of refractory materials

The general requirements of a refractory material can be summed up as:

1. Its ability to withstand high temperatures with sudden changes of temperature.
2. Its ability to withstand action of molten metal, hot gasses and slag erosion etc.
3. Its ability to withstand load at service conditions.
4. Its ability to resist contamination of the material with which it comes into contact.
5. Its ability to maintain sufficient dimensional stability at high temperatures and after/during repeated thermal cycling.
6. Its ability to conserve heat.

Classification of Refractories

Refractories are classified into number of ways on the basis of chemical properties of their constituent substances, their refractoriness, method of manufacture and physical form.

1) Classification Based on Chemical Composition

Refractories are typically classified on the basis of their chemical behavior, i.e. their reaction to the type of slags. Accordingly the refractory materials are of three classes - Acid, Basic & Neutral.

Acid Refractories:

Acid refractories are those which are attacked by alkalis (basic slags). These are used in areas where slag and atmosphere are acidic. Examples of acid refractories are:

1. Silica (SiO_2).
2. Zirconia (ZrO_2).
3. Aluminosilicate.

Neutral Refractories:

Neutral Refractories are chemically stable to both acids and bases and are used in areas where slag and atmosphere are either acidic or basic. The common examples of these materials are:

1. Carbon graphite (most inert)
2. Chromites (Cr_2O_3)
3. Alumina

Out of these graphite is the least reactive and is extensively used in metallurgical furnaces where the process of oxidation can be controlled.

Basic Refractories:

Basic refractories are those which are attacked by acid slags but stable to alkaline slags, dusts and fumes at elevated temperatures. Since they do not react with alkaline slags, these refractories are of considerable importance for furnace linings where the environment is alkaline; for example non-ferrous metallurgical operations. The most important basic raw materials are:

1. Magnesite (MgO) - caustic, sintered and fused magnesite
2. Dolomite (CaO.MgO) - sintered and fused dolomite
3. Chromite -main part of chrome ore

Special Refractories:

These are expensive refractory materials which have been manufactured using synthetic (Fused/Sintered) grains free from impurities under highly controlled production parameters. They are used for special purpose like- construction of crucible, some parts of furnaces and R&D purpose etc. where the cost of refractory is of no consideration. They include materials like – Pure Alumina, Sialons (Si-Al-O-N) Thoria (ThO_2), Beryllia (BeO), Zirconia, Boron Nitride, Spinel etc.

Insulating materials

Insulating materials are high porosity refractories with low thermal conductivity used in order to reduce the heat losses. Insulating materials have a lower density and offers higher thermal resistance compared to firebricks. In all cases, thermal conductivity of the insulation increases significantly as temperature increases. Wide ranges of insulating refractories with wide combinations of properties are now available. It is likewise cheaper in contrast to the high duty bricks

2) Classification Based on Method of Manufacture

The refractories can be manufactured in either of the following methods:

- a) Dry Press Process.
- b) Fused Cast.
- c) Hand Molded.
- d) Formed (Normal, Fired or chemical bonded).
- e) Unformed (Monolithic – Plastics, Ramming mass, Gunning, Cast able, Spraying).

3) Classification Based on Physical Form

Refractories are classified according to their physical form. These are the shaped and unshaped refractories. The shaped is commonly known as refractory bricks and the unshaped as “monolithic” refractories.

Properties of Refractories

Important properties of refractories are: chemical composition, bulk density, apparent porosity, specific gravity and strength at atmospheric temperatures. These properties are often among those which are used as control points in the manufacturing and quality control process.

Some of the important characteristics of refractories are:

1) Melting Point:

Melting temperatures (melting points) specify the ability of materials to withstand high temperatures without chemical change and physical destruction. The melting point of few elements that constitute refractory composition in the pure state varies from 1716°– 3482°C

2) Size and Dimensional Stability:

The size and shape of the refractories is an important feature in design since it affects the stability of any structure. Dimensional accuracy and size is extremely important to enable proper fitting of the refractory shape and to minimize the thickness and joints in construction.

The contraction or expansion of the refractories can take place during service. Such permanent changes in dimensions may be due to:

- 1. The changes in the allotropic forms which cause a change in specific gravity.
- 2. A chemical reaction which produces a new material of altered specific gravity.
- 3. The formation of liquid phase.
- 4. Sintering reactions.
- 5. It may also happen on account of fluxing with dust and slag or by the action of alkalis on fireclay refractories, to form alkali-alumina silicates, causing expansion and disruption.

The linear change can be calculated on basis of volume change by the following relationships:

$$\text{Final Volume} - \text{Original Volume}$$

$$\text{Volume Change \%} = \frac{\quad}{\text{Original Volume}} \times 100$$

$$\text{Linear Change \%} = \frac{\text{Final Length} - \text{Original Length}}{\text{Original Length}} \times 100$$

3) Porosity and Slag permeability

Porosity is a measure of the effective open pore space in the refractory into which the molten metal, slag, fluxes, vapors etc. can penetrate and thereby contribute to eventual degradation of the structure. The porosity of refractory is expressed as the average percentage of open pore space in the overall refractory volume.

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

High porosity materials tend to be highly insulating as a result of high volume of air they trap, because air is a very poor thermal conductor. As a result, low porosity materials are generally used in hotter zones, while the more porous materials are usually used for thermal backup. Refractory materials with high porosity are usually NOT chosen when they will be in contact with molten slag because they cannot be penetrated as easily.

True porosity of a refractory brick is the percentage of the volume of combined open and close pore space of its total volume. Density of a refractory brick is controlled by both open and close pores while its permeability is affected by only open (i.e., interconnected) pores.

Porosity determination:

In raw/green refractory materials the pores are all open fluids can pass through them. When these materials are fired some liquid formation due to fusion takes place and as a result some pores will be sealed. The apparent porosity as such takes the open pores and not the closed pores. True porosity is defined as:

$$\text{True porosity} = \frac{\text{Volume of open pores} + \text{Volume of closed pore}}{\text{External Volume}} \times 100$$

$$\text{Apparent porosity} = \frac{\text{Volume of open pores}}{\text{External Volume}} \times 100$$

With increase in the porosity of the refractory bricks, its

- Thermal conductivity decreases because the air which fills the pores acts as an insulator, which is why insulating bricks have higher porosity.
- Resistance to the penetration of metal, molten slag and flue gases reduces due to increased permeability.

- Temperature fluctuation sensitivity reduces as pores can accommodate the thermal expansion due to heat.
- Strength reduces due to decreased compactness obviating their usage in taller structure demanding higher strength.

4) Density:

The bulk density is generally considered in conjunction with apparent porosity. It is a measure of the weight of a given volume of the refractory. For many refractories, the bulk density provides a general indication of the product quality; it is considered that the refractory with higher bulk density (low porosity) will be better in quality. An increase in bulk density increases the volume stability, the heat capacity, as well as the resistance to abrasion and slag penetration.

True density is the weight per unit volume of the refractory including the volume of its open and close pore space.

Determination of Bulk Density:

The bulk density of any refractory is measured by the equation:

$$\text{Bulk Density} = \frac{\text{Total Weight}}{\text{Total volume}} \quad \text{of refractory}$$

5) Refractoriness

Refractoriness of a refractory is the temperature at which is the material softens and hence is the measure of fusibility of the material. Addition of an impurity in the refractory material lowers its fusion point/refractoriness depending upon the amount of impurity present, the melting point of the lowest fusing constituent and the capacity of the lowest fusing constituent to dissolve the material of higher fusion point at comparatively low temperature.

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.

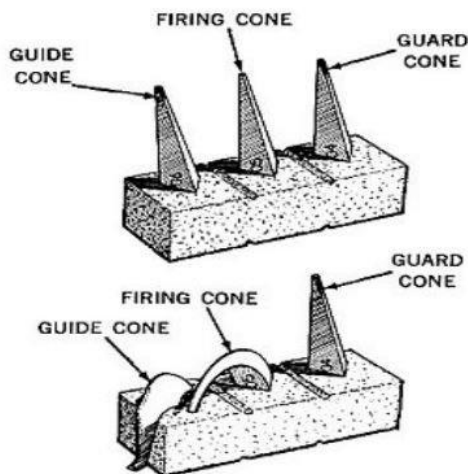
6) Pyrometric Cone Equivalent (PCE)

"Fusibility temperature range" is a more appropriate term for refractory materials as mixture of refractory materials do not have a sharp fusion/melting point. The heat resistance of refractory material is expressed in terms of Pyrometric Cone equivalents (PCE) which is determined by comparing the softening of a test pyramid cone with that of standard pyramid cones of known fusion temperature by heating them under similar conditions.

Temperature at which a refractory will deform under its own weight is known as its softening temperature which is indicated by PCE. Refractories due to their chemical complexity melt progressively over a range of temperature. Hence refractoriness or fusion point is ideally assessed by the cone fusion method. The equivalent standard cone which melts to the same extent as the test cone is known as the pyrometric cone equivalent (PCE).

Thus in the figure (1) refractoriness of sample A is much higher than B and C. The pyrometric cone equivalent indicates only the softening temperature. But, in service the refractory is subjected to loads which would deform the refractory at a much lower temperature than that indicated by PCE. With change in the environmental conditions, such as reducing atmosphere, the P.C.E. value changes drastically.

The standard cones are called 'Segar cones' (as Germany standard) and 'Orton cones' (as British standard) and they are numbered according to their refractoriness/fusion points.



7) Refractoriness Under Load (RUL):

The refractoriness under load test (RUL test) gives an indication of the temperature at which the bricks will collapse, in service conditions with similar load.

Refractoriness under load (RUL) of a refractory material is a measure of its failure resistance to the combined action of heat and load. RUL is the softening temperature of a refractory brick (indicated by breaking of the test specimen) when a load of 2 kgf/cm² is applied as per the standard test procedure.

Refractory bricks generally having more than two constituent compounds fail under load conditions at much lower temperature (i.e., at RUL) than the fusion point (i.e., refractoriness) of the highest melting and predominant constituent. That signifies that the temperature corresponding to the refractoriness under load of a refractory brick is much lower than its refractoriness (fusion/melting point). A refractory material composed of a single pure compound will have a closer value of its refractoriness and refractoriness under load.

Refractory failure is also influenced by its exposure time to load and heat. Longer exposure time results in failure of refractory under relatively low load and temperature conditions. Similarly refractories will fail at a lower temperature with increased load.

8) Strengths:

The physical strengths, in both cold and hot conditions is important and are often characterized as measures of the use of a refractory. Cold strengths indicate the handling and installation of the refractory, whereas hot strengths indicate how the refractory will perform when used at elevated temperatures. Initial strength develops in refractory materials during the forming process. For shaped refractories, the strengths often develop during the physical processing of the products and sometimes followed by higher temperatures where the refractory goes through a firing process. For monolithic refractories, the initial strength develops during the installation or forming process (for precast shapes), and the final strength develops while in application.

9) Thermal Properties:

a) Thermal Conductivity:

Thermal conductivity is defined as the quantity of heat that will flow through a unit area in direction normal to the surface area in a defined time with a known temperature gradient under steady state conditions. Thermal conductivity (k) is directly proportional to the heat capacity (C), the quantity and velocity of the carrier (v) and the mean free path (λ):

$$K \propto C v \lambda$$

Increasing the heat capacity; increasing the number of carriers and their velocity and increasing the mean free path (decreasing scattering) result in increased thermal conductivity

Thermal conductivity depends upon the chemical and mineralogical compositions as well as the glassy phase contained in the refractory and the application temperature. The conductivity usually changes with rise in temperature. In cases where heat transfer is required through the brick work, for example in regenerators, muffles, etc. the refractory should have high conductivity. Low thermal conductivity is desirable for conservation of heat by providing adequate insulation. After firing process of refractories, the inner structure contains three phases (crystal phase, glass phase and gas phase (pores)).

Effect of the structure and the microstructure of refractories on the thermal conductivity:

1. The highest conductivity are achieved in the cluttered structure, that in structures consisting of single element, structure made up elements of similar atomic weight, and structure with no extraneous atoms in solid solution. Graphite is good example of single element refractory structure having high thermal conductivity.
2. Refractories composed of elements of similar atomic weight and size, having high thermal conductivity. Good examples of this type of refractory are BeO, SiC and B₄C. While the refractories have large different in atomic weight and size have low thermal conductivity as example UO₂ and ThO₂.
3. Impurities, porosity and microcracks exert the main influence on the effective thermal conductivity. Presence of these defects can reduced the thermal conductivity of refractories.

A more porous brick has, in general, lower thermal conductivity. However, the size and number of the pores is also important as heat transfer can take place across the pores by radiation and is prominent at high temperature.

Refractories used in melting furnace should have low thermal conductivity to ensure least heat losses and maximum heat efficiencies whereas recuperates require refractory with high thermal conductivity to ensure maximum heat transfer.

b) Thermal Spalling

Spalling is defined as the fracture of the refractory brick or block due to any of the following causes:

- A temperature gradient in the brick due to uneven heating or cooling that sets up stresses causing failure. (Thermal Spalling).
- Compression in a structure of refractories due to expansion of the whole from a rise of temperature causing shear failure.
- Variation in coefficient of thermal expansion between the surface layer and the body of the brick, due to the surface slag penetration or to structural changes in service resulting in shearing off the surface layer. As a general rule, those with a lower thermal expansion co-efficient are less susceptible to thermal spalling

Thermal Spalling can be reduced by:

- Using materials with low coefficient of expansion and avoiding sudden temperature fluctuation for example addition of alumina in small quantities decreases expansion to a large extent.
- Using high porosity bricks.
- By designing the furnace such that stress is alienated.

c) Thermal Diffusivity

Thermal diffusivity is the thermal conductivity divided by density and specific heat capacity at constant pressure. It measures the ability of a material to conduct thermal energy relative to its ability to store thermal energy. It has the SI unit of m^2/s or m^2/hr .

d) Thermal Expansion

This is a measure of the refractory about its linear stability when it is exposed to different ranges of high temperatures and then cooled to room temperatures. It is defined as a permanent linear change (ASTM C-113) and is measured by the changes in the longest linear dimensions. Most refractory materials expand when heated. Hence, when refractories are installed at room temperatures, the whole structure tightens up when heated.

d) Thermal Shock

Thermal shock is the fracture of a body resulting from thermal stresses induced by rapid temperature changes. Because ceramic materials are brittle, they are especially susceptible to this type of failure. The thermal shock resistance of many materials is proportional to the fracture

strength and thermal conductivity, and inversely proportional to both the modulus of elasticity and the coefficient of thermal expansion.

Thermal shock is an important property for a refractory material. Most high-temperature processes experience heating and cooling. Thermal shock can be indicated by the number of cycles to withstand such temperature fluctuations. Thermal shock resistance can be defined as partial or complete fracture of material due to gradient temperature. The factor that affects the thermal shock resistance includes the shaping methods and the firing temperatures.