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THE SCOPE OF HIGH TEMPERATURE INORGANIC INDUSTRIES

1.1 Introduction

High temperature inorganic industries are concerned with the manufacturing of **ceramic products**. Ceramics have been traditionally produced since several millennia in diverse parts of the world such as ancient Egypt, China and Greece etc. … They were produced by firing to a high temperature a mixture of earthly materials such as clays, sand ,…Since then, ceramics have always been regarded as the product of firing to an elevated temperature a mixture of silicate based materials. Recently, however, some ceramic products could be prepared from non-silicate raw materials and sometimes even without firing. That is why the traditional view towards ceramics has changed so that nowadays a ceramic material is defined **- metallic solid.**

There are many ways to classify ceramic products. We have chosen in this text the classification according to use. In this respect, we have to differentiate between traditional ceramics, which are based on silicate raw materials and modern ceramics which do not necessarily contain silicates.

1.2 Traditional Ceramics

1.2.1 Pottery

These represent a category of ceramic products that include traditional pottery, dinnerware, and various types of porcelain: chemical, electrical, etc. All these products are manufactured using three main raw materials, namely, clays, fine sand and a fluxing agent such as feldspar. That is why; they are often referred to as **triaxial bodies**. The difference in their appearance is mainly due to the purity of the raw materials and the temperature to which they are fired.

Porcelains represent the purest form of pottery, known as whitewares. They are characterized by a white color, almost zero porosity and translucent appearance. Among their products are high quality dinnerware, chemical ware and electrical insulators. They are usually produced in a final glazed form. On the other hand, stoneware products are characterized by low porosity (< 3%), a whitish color and an opaque appearance. Typical such products are "porcelain" tiles, high quality sanitary ware and medium quality dinnerware. The products of least quality in this category are called earthenware, such as cheap dinnerware and sanitary ware. These are characterized by being colored (owing to the presence of impurities such as iron oxides), opaque and are always glaze coated. Figure (1.1) shows the location of products in triaxial bodies on a composition diagram.

1.2.2 Refractory products

These are ceramic products intended for use under high temperature conditions, particularly in furnaces. They can be produced into brick shape or as a monolithic powder or as special shapes to suit the application such as tubes, nozzles, etc. They have to withstand high temperature, and often, high abrasion due to slag action (as in metallurgical furnaces). They should be chemically inert and have a reasonable mechanical strength on use.

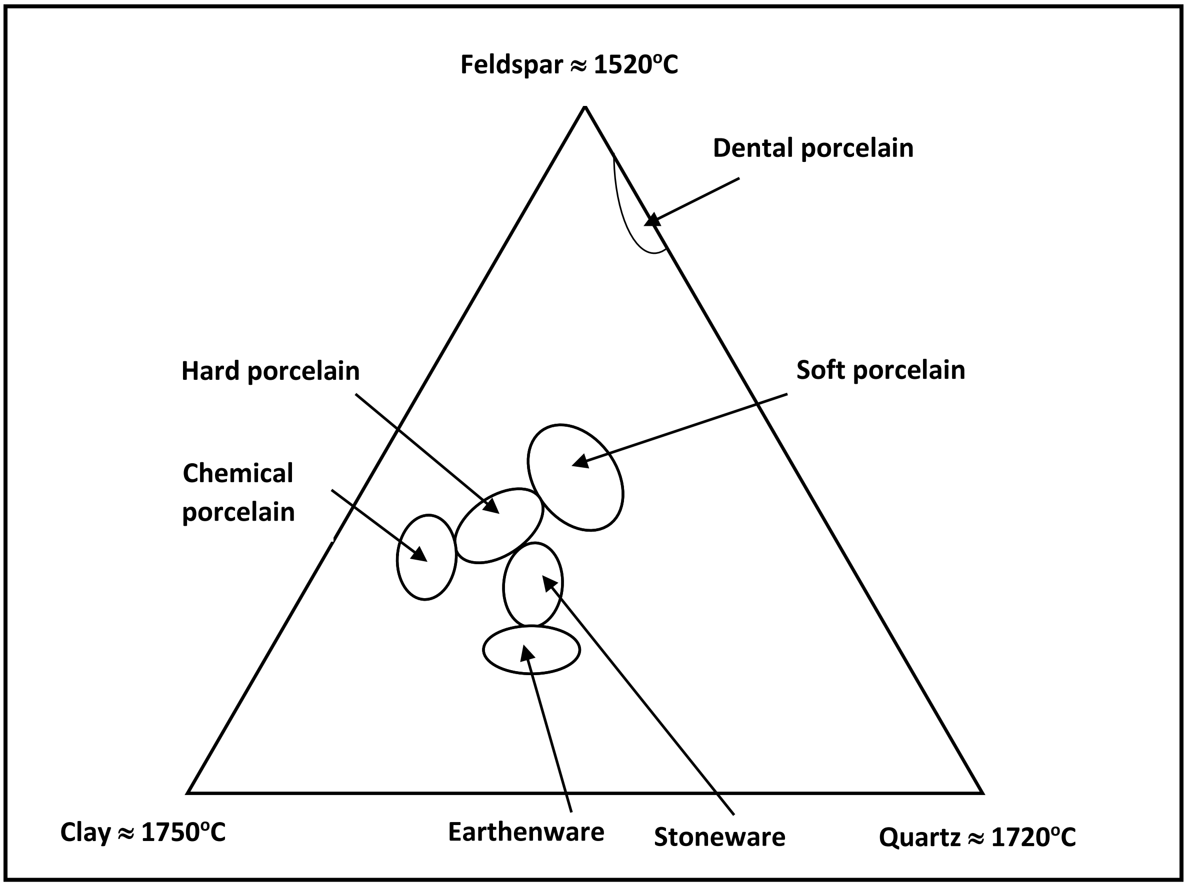

Fig 1.1 Location of triaxial bodies products on the composition diagram (Temperatures represent approximate melting points)

1.2.3 Structural clay products

These are ceramic products mainly used in the building industry such as bricks, blocks, sewer pipes etc. … These products are manufactured from clay and fine sand, and occasionally fluxing materials. In some cases, local waste can be incorporated into the mix, such as cement dust, quarry refuse, blast furnace slag etc. … the main purpose of such additions being economical. They are usually fired to high temperatures into a variety of kilns.

1.2.4 Glasses

Glasses are under cooled liquids. As a glassy melt is cooled, its viscosity increases to such an extent that crystal formation is not possible. They are rigid at low temperatures but gradually soften as temperature is raised. Below a certain temperature known as **the glass transition temperature T_t**, the rigid material formed has a volume expansion coefficient comparable to solids, Figure (1.2).

Whereas the melting point of a certain solid is a constant value, the transition temperature is not constant and depends on the past history of the melt and the rate of cooling.

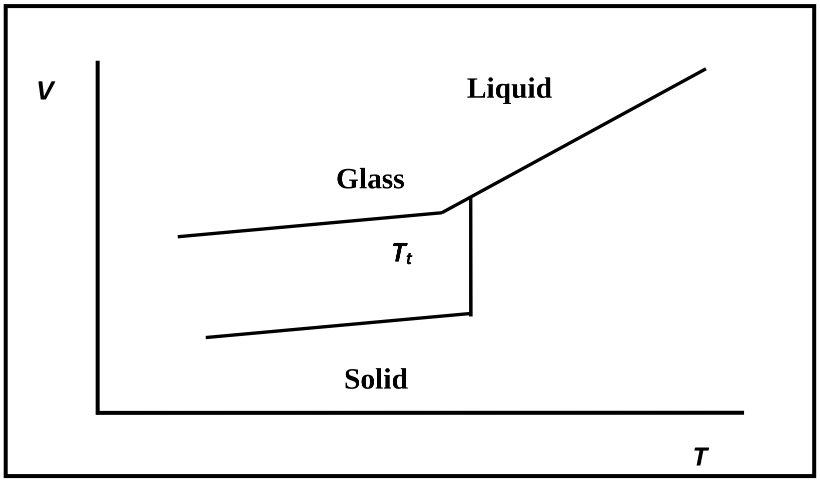

Fig 1.2 Cooling of a glass and a crystalline solid

1.2.5 Cementing materials

Cementing materials are classified as simple or complex cements. The former do not radically change in chemical composition as they set by the action of an external agent, usually water. For example, quick lime (CaO) will convert to slaked lime $Ca(OH)_2$ on water addition. Similarly, Plaster of Paris ($CaSO_4.\frac{1}{2}H_2O$) will convert to Gypsum ($CaSO_4.2H_2O$).

On the other hand, Portland cement is manufactured from a mixture of clay (Aluminum silicate hydrate) and limestone ($CaCO_3$) fired to a high temperature. The product of firing has a totally different composition than the parent raw materials, being constituted of calcium silicates and calcium aluminate. This is an example of a **complex cementing material**.

1.2.6 Glazes and Enamels

A **glaze** is a glassy coat applied on a ceramic surface such as dinnerware, wall tiles, porcelains, sanitary ware. They are classified into three main types:

Raw glazes are prepared by direct firing of the reactants, followed by their suspending in water to form a slurry, then applying to the ceramic surface. The glazed ware is to be subsequently fired in a kiln.

Fritted glazes are prepared from raw materials that can produce on firing water soluble oxides or sometimes poisonous oxides (such as PbO). In order to stabilize such oxides, the raw materials are melted then quenched into cold water to produce glassy lumps known as **frit**. These are finely ground, usually in ball mills, where some necessary additions are also made. The product is water insoluble and can thus be suspended in water. It is then applied onto the ceramic surface followed by firing.

Salt glaze is applied on some ceramic products, such as sewer pipes and pots, by simply throwing common salt and borax in the furnace where these articles are being fired. At the elevated temperature prevailing, these salts vaporize and react with silica and alumina on the external surface of the fired products to form sodium boro-alumino silicates in a molten state. These, on cooling, will seal off the open pores of the product.

Enamels, on the other hand, are glassy coatings to cover metallic surfaces like steel, aluminum, … .They protect the metallic surface against possible corrosion or abrasion besides serving a decorative purpose, as different colors may be used. Their composition differs from that of glazes in that their melting point should be lower than that of the metal on which they are applied.

1.3 Modern Ceramics

1.3.1 Non-silicate refractory materials

Nowadays, there are a considerable variety of refractory products that are not silicate based. Examples are alumina, zirconia, magnesia, thoria refract- ories. These withstand very high temperature and are used in some industries where chemical corrosion and mechanical abrasion prevail. For example, magnesite refractories are commonly used in the clinkering zone of cement kilns. In the glass industry, tank kilns can be lined with zircon refractories.

1.3.2 Abrasive ceramics

These represent a category of products that are extremely hard. These are used in the manufacture of cutting tools, grinding wheels and special polishing powders. The most important of these products are **corundum** which is very pure aluminum oxide and **silicon carbide** commercially known as **carborundum.** Also, **silicon nitride** is a hard refractory material that is used in the manufacture of cutting tools and in the manufacture of different components of ceramic engines, such as piston heads. Figure (1.3) shows a series of ceramic gears made out of stabilized zirconia (ZrO_2 + 4% Y_2O_3) and used in moving motor parts operating under severe conditions.

An important class of hard ceramic materials is that of ceramic – metal composites, also known as **cermets**. These are manufactured by bonding together hard ceramic grains (such as SiC or Si_3B_4) using a metal (Fe or Ni, etc.). They are used in the manufacture of ceramic valves to regulate molten metal flow and in spacecraft applications.

Fig 1.3 Ceramic gears

1.3.3 Magnetic ceramics

This class of materials is characterized by special crystal structures that impart to them special magnetic properties.

The first category of magnetic ceramics comprises **Hexagonal ferrites** or **Hard ferrites.** These have general formula: $MO.6Fe_2O_3$, such as $BaO.6Fe_2O_3$ and $PbO.6Fe_2O_3$. They are hard to demagnetize, hence their name. Since those materials are hard to demagnetize, they are considered as excellent permanent magnets that are used in loudspeakers, in DC motors and are often embedded in a polymer matrix to form **plastic magnets**.

A second type of ceramic magnets is known as **Soft ferrites**. These have a structure known as the **Spinel** structure typical of ferrites having the composition MFe_2O_4 ($MO.Fe_2O_3$) such as $NiFe_2O_4$, $MnFe_2O_4$ or even Fe_3O_4 ($FeO.Fe_2O_3$). They are characterized by a **narrow hysteresis loop**. They can be easily demagnetized. The field of application of soft ferrites includes both high and low frequency applications, microwave circuits and on-off computer circuits.

Generally the magnetic properties of all ferrites will exhibit serious change if they are heated above a temperature known as the **Curie point**. In this respect, a third type of magnetic ceramics known as **Garnets** is not easily affected by a rise in temperature. They have the general formula $M_3Fe_2Fe_3O_{12}$, where M is a rare earth element, like yttrium (Y).

1.3.4 Ceramics with special electrical properties

(a) Piezoelectric ceramics

A piezoelectric material is a material which, when subjected to an external stress will produce an electric current. Conversely, when such a material is placed in an electric field, a mechanical strain will develop.

The origin of such behavior has to be traced to the structure of the material crystals. If the position of atoms in a lattice is such that the resultants of positive and negative charges do not coincide, the material will behave as a **dipole**. A dipolar crystal, under the influence of an external field, will tend to produce a positive or negative strain according to the direction of the applied field (Figure 1.4).

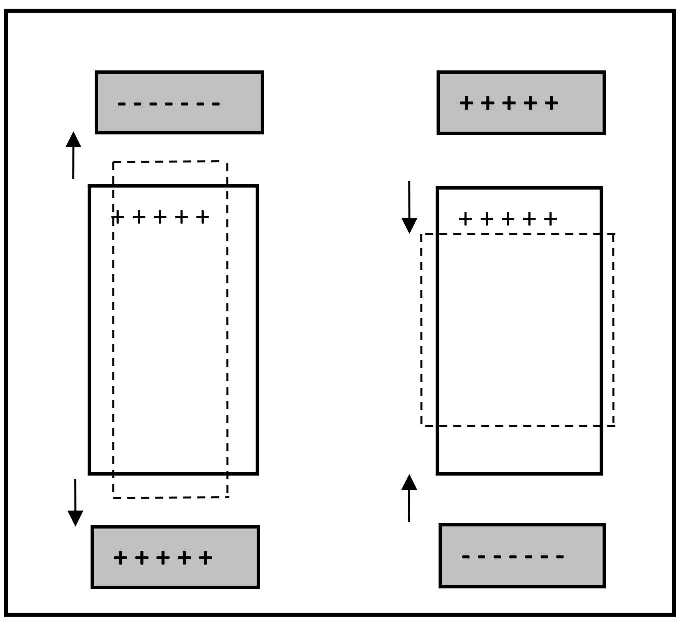

Fig 1.4 Piezoelectric effect in ceramic crystals

The situations shown in Figure (1.4) are restricted to single piezoelectric crystals. In the case of a polycrystalline material, however, the orientations of the dipoles are random and no net effect can be observed. That is why the material has first to be subjected to a strong electric field to cause the orientation of all crystals. This process is called **poling**.

The first piezoelectric ceramic material to be used was quartz about sixty years ago. Since then, many more materials were synthesized that showed a more pronounced effect, such as $BaTiO_3$, $PbTiO_3$, $(Pb,Zr)TiO_3$…Some applications of such materials are quartz watches, firearms, sensors etc. …

It is also worth noticing that most piezoelectric ceramics also display the **pyroelectric effect**. That is, if subjected to a change in temperature will develop an electric field due to spontaneous polarization.

(b) Dielectric ceramics

There is a diversity of ceramic materials displaying electrical properties. Among such materials are dielectrics. A dielectric material will not conduct electricity. However, under the influence of an external field, there occurs a charge polarization such that a short range movement of charges takes place. This has for effect to store part of the charge as the field is removed. That is why dielectric ceramics can be used as capacitors. A typical example is $BaTiO_3$ and similar materials. If the capacity of a non-conductive ceramic material to store electric charge is very low, then it will be used as an electrical insulator. Typical insulators are AlN that is used in electronic applications and alumina, used in the manufacture of spark plugs.

1.3.5 Bioceramics

Ceramic materials have proved to be an excellent choice for bone pros-theses. This is because of their chemical inertness, their non-thrombogenic and their non-carcinogenic properties. Among the most promising materials are: synthetic hydroxyapatite (a type of calcium phosphate) and calcium aluminate.

1.3.6 Glass ceramics

If a glass melt is cooled, it does not usually form crystals. Under some circumstances, however, controlled crystallization can take place, by proper heat treatment. The product consists of crystals embedded in a glassy matrix. These products, also known as **pyrocerams** have excellent resistance to thermal shock and are used in the manufacture of ovenware. Glass ceramics can also be used for decorative purposes in what is known as **glass bricks**. Figure (1.5)

Fig 1.5 A glass brick

1.3.7 Non silicate glasses

These types of glasses have a high refractive index. They are mainly borate, rather than silicate based. They are used in the manufacture of lenses. Their use has allowed for the production of thin lenses even in cases of strong short or long sighting.

Another type of such glasses is the **chalcogenide** category which includes compounds such as GaSbTe and AgInSbTe that are used in the manufacture of fiber optics, infrared lenses and fibers, optical disks etc.

1.3.8 Molecular sieves

These are complex inorganic molecules either natural or synthetic composed of SiO_2, Al_2O_3, Na_2O,…that have a bee hive – like structure with openings in the nanometer range, Fig.(1.6). They are used to separate fluids according to their molecular weight, particularly in the oil industry.

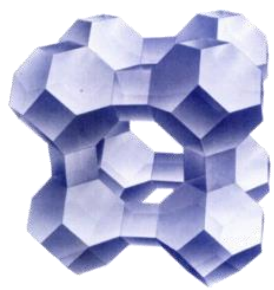

Fig 1.6 Structure of a molecular sieve

1.3.9 Nuclear ceramics

This category comprises ceramic materials used in nuclear applications. For example, uranium dioxide and uranium carbide are used as nuclear fuels and BeO is used as a neutron moderator in fission type reactors. In fusion type reactors, Li_2ZrO_3 is used as a tritium breeder, while Si_3N_4 and B_4C_3 are used as refractory materials for the internal lining of the reactor.

1.3.10 Ceramic nanomaterials

These are materials having particle size in the nano range (10^{-9}m), generally accepted as ranging from 1 to 100 nm.

Since the surface to volume ratio of any powder is inversely proportional to its particle size, such materials have extremely high specific surface areas. Besides, since their size is comparable to atomic sizes, a large fraction of their atoms lie on the surface, resulting in more surface dependent properties. For example, some nanosized metallic powders are excellent catalysts. Also, the extremely low particle size leaves their structure with practically no defects. This means much better mechanical, electrical and magnetic properties.

Suggested additional reading

1. W.D. Kingery, H.K. Bowen, D.R. Uhlmann, *Introduction to Ceramics,* 2nd ed., J. Wiley & Sons, N.Y., 1976
2. R.J. Brook, Ed., *Concise Encyclopedia of Advanced Ceramic Materials*, Pergamon, N.Y., 1991
3. M.W. Barsoum, *Fundamental of Ceramics,* 1st ed., McGraw-Hill, Singapore, 1997
4. Y.M. Chiang, D.Birnie III, W.D. Kingery, *Physical Ceramics,*1st ed., J. Wiley & Sons, N.Y., 1997
5. R.C. Buchanan *Ceramic materials for electronics,* 3rd edition, R.C. Buchanan, 2004

Suggested sites

Piezoelectric ceramics: https://www.youtube.com/watch?v=4nbBAG-848c

Bioceramics: https://www.youtube.com/watch?v=Gmt7X_nqh-Q