Science and Technology of Ceramics

1. Traditional Ceramics

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Ceramics can be classified broadly as traditional and advanced. Ceramics made from naturally occurring raw materials and without much processing are the traditional ceramics. These ceramics are widely used all over the world.

Materials: An Introduction

Since very early days, man has been using materials available around him to improve his lifestyle. The ages or periods, in fact, have been named after the main material that was being used during that period, for example, the stone-age, iron-age, copper-age or plastic-age! Man learnt to shape the materials in the form of weapons, cooking-ware, building materials etc.. Mixing two elements to improve the properties of individual elements came into vogue, which opened up the whole field of alloy science and technology. Though the periodic table consists of more than 100 elements, very few of them are being used in their pure form. The elements can be broadly classified as metals, semiconductors and insulators (non-metals). Elements of the groups I and II, transition and rare-earth elements are all metallic. Some elements of the IV group are found to be semiconducting and the rest of the elements of the periodic table are non-metallic. Elemental materials will not be discussed in this article.

Living things are made up of only a few elements like C, H, N and O in combined forms; nature has synthesized an abundant number of compounds using just these few elements. The need and ingenuity of man has also come into its own in synthesizing compounds which are not found in nature. Organic chemists, for instance, have synthesized hundreds of thousands of new compounds over the years. Many of these compounds synthesized in the early part of this century were directed at either scientific curiosity or to find applications in pharmaceuticals, dyes, artificial fibers and the like. Even inorganic synthesis was seldom aimed at replacing the role of metals and other traditional materials of daily use. However, in the last several decades this picture has changed. There has been a conscientious effort to synthesize materials with desired physicochemical properties for specific applications. With this, the area of materials science and technology influenced every segment of our day to day life like housing, clothing, food production, transportation, communication etc. Elements are, largely, reacted or alloyed with each other. Thus, a wide variety of compounds and alloys can be formed with a wide range of properties. Some of the properties can be tailored by mixing the right kind of elements in right proportions for the required applications. Compounds can be broadly classified as polymers and ceramics. Here the discussion will be restricted to mainly the scientific and technological aspects of ceramic materials only. The article has been divided into three parts for easy reading.

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Ceramics

The word ceramics comes from the Greek word 'keramos' which means potter's earth. Ceramics cannot be defined in a very simple fashion. Ceramics are usually associated with pottery, sanitary ware, tiles etc. Though this is not incorrect, it is incomplete. One of the definitions is 'solid compounds which are formed by the application of heat and pressure (if necessary) comprising two or more elements, metals or non metals'. This class shelters a large number of compounds under its umbrella. We have a whole lot of materials with different electrical properties (like metallic, semiconducting and insulating ceramics) and mechanical properties (soft, hard and superhard materials). Structurally these materials are either crystalline or amorphous (glassy). In crystalline materials, the unit cells are arranged in a definite sequence along all three directions or in other words, there is a long range ordering. In amorphous ceramics, there is only local ordering of the unit cells, which is also called short range ordering. Compounds in single crystalline form are not classified as ceramics here. Hence

Intrinsic properties are determined by the structure at the atomic scale and are not severely altered by modification of the microstructure. Examples of intrinsic properties are melting point, coefficient of thermal expansion, elastic modulus etc.

semiconducting applications, where even though compounds are used they are in the form of single crystals, are not considered here. Similarly applications which involve carrying high current densities also require single crystals.

Intrinsically[1], ceramics have a high melting point and they are hard, brittle and chemically inert. The main features of ceramics are:

1. The presence of strong covalent character of chemical bonding. The high strength of the covalent bond is responsible for the general high melting point of ceramics, their brittleness, good corrosion resistance, low thermal conductivity and high compressive strength. The enormous range of electronic and magnetic properties of ceramics is the manifestation of slight variations in the chemical bonding.

[2] Microstructure refers to the nature, quantity and distribution of the structural elements or phases in the ceramic.

2. Microstructures[2] comprising inorganic crystalline compounds and/or amorphous glass in varying proportions.

3. Processed at high temperatures. High temperature processing in ceramics is important as chemical reactions are accelerated and many raw material constituents of ceramic bodies decompose at high temperatures and form more stable compounds. High temperatures are also necessary to produce new crystal compounds and form homogeneous solid solutions (*Box* 1). Reactions that produce a liquid phase become more rapid at elevated temperatures and also quenching of a liquid phase from high temperature is necessary to produce most glass-ceramics. Thermal

Box 1.

Solid solution is a homogeneous crystalline phase, which contains more than one chemical species. Here one should note that any crystal is made up of a lattice and a base. A lattice is a regular array of points in space. Basis is the atom or molecule that occupies the lattice points. In solid solutions, instead of a single kind of basis, we could have two (or more) kinds of basis atoms or molecules distributed randomly on the lattice points. For example, an alloy like 22 carat gold is a solid solution of copper and gold. In molecular solid solutions, two types of molecules occupy the lattice points randomly. Usually solid solutions are formed from two components with similar crystal structures.

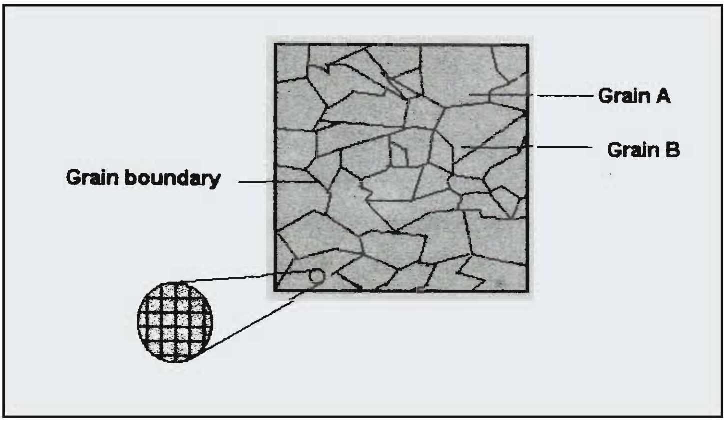


Figure 1. Schematic representation of grains and grain boundaries in a ceramic material. Each grain is made up of many single crystals.

processing also increases the density of ceramic objects as porosity is gradually eliminated and inter-granular bonds are strengthened.

Grain Boundaries

A polycrystalline solid is composed of a collection of many small sized single crystals called grains. Areas of disorder known as grain boundaries (*Figure* 1) separate these grains from one another. In ceramics the grains are visible only under a microscope. The grains in a solid are of various sizes and shapes. The presence of these grains along with porosity is called the microstructure. There are many properties of ceramics like Young's modulus, melting point, etc., which are independent of the microstructure. However, some of the properties are highly sensitive to the grains, their sizes and the grain boundaries. Conduction of ions or electrons is impeded at a grain boundary due to the lattice mismatch. Because of this the conductivity in a polycrystalline material will be lower than in a single crystal by, quite often, an order of magnitude. Similarly, some of the mechanical properties of ceramics like hardness, high temperature strength, and creep resistance is microstructure dependent. Hence it becomes important to tailor the microstructure of the components as required for the application. Many syntheses and sintering (*Box* 2) techniques have been developed to control the microstructure of the ceramic component obtained. During sintering a general coarsening of

Box 2.

Sintering is a process where the ceramic compact is heated at high temperatures for long durations of time. In many cases heating may be done for four days or more. By doing so, the grains in the ceramic grow in size decreasing the porosity in the compact.

the microstructure by grain growth occurs. Also, the average *grain size increases with sintering time and larger ones for* growing bigger consume the smaller grains. The final ceramic compact[3] contains some residual porosity and grains that are much larger than the starting size of the particle. The important factors that control sintering are the temperature of sintering, the green density[4], uniformity of green microstructure, the atmosphere in which sintering is done, the presence of impurities etc. *Sintering under pressure is also done to eliminate the* porosity. Another way of sintering is by the liquid phase sintering. In this process a proportion of the material being sintered is in the liquid phase and because of this uniform densities can be achieved in the final compact.

[3] A ceramic compact is a sintered ceramic body of a definite shape and size.

[4] Green density is the density of the compact of the starting materials before the reaction.

[5] *Rocks can be classified as* sedimentary and igneous rocks. Sedimentary rocks are the result of accumulations of debris and sediment derived from the breakdown of pre-existing rocks by the action of weather. The sediments are usually laid down under water *in streams, rivers, lakes and* seas (usually sand stones, limestones and clays). Igneous rocks are formed from the cooling of molten material forced from beneath the solid layers of the earth's crust into the outer layers. Examples are volcanic rocks (basalt) and *plutonic rocks (granite).*

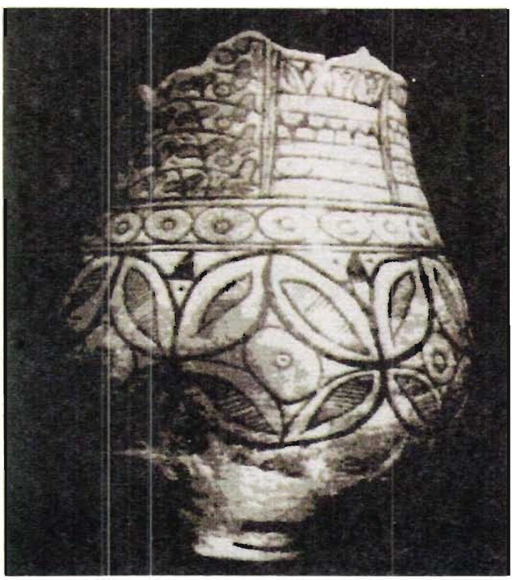
Ceramics can be broadly classified into two groups:

1. Traditional ceramics
2. Advanced ceramics.

Traditional Ceramics

Traditional ceramics are made from naturally occurring raw materials. Right from the dawn of civilization, clay has been used to make pots and other articles. Clay, when mixed with water, becomes easily mouldable into any shape and size. Man then discovered that these clay pre-forms could be fired to harden them. Later, he also learnt the art of glazing, which closed the pores of the ceramic pots making them watertight. The artistic temperament and skills of people began to come to light. Pottery, belonging to ancient civilization, painted in beautiful colors and designs can be seen in museums. An earthen jar found from Harappan era is shown in *Figure* 2.

Figure 2. A ceramic jar from Harappan era.



The clays come under the sedimentary rocks[5]. More than a dozen minerals have clay-like properties, and the building-clays contain

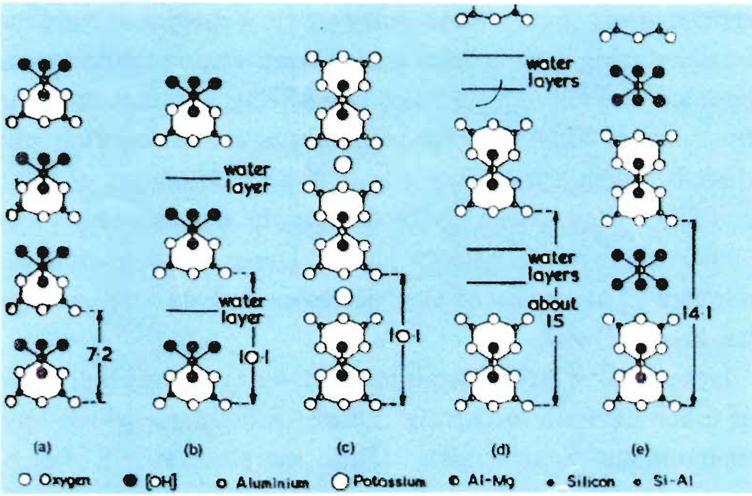


Figure 3. Schematic representation of layers of clays: a) kaolinite, b) hydrated halloysite, c) muscovite, d) hydrated montmorillonite, e) chlorite.

primarily kaolinite, montmorillonite and illite types occurring together or separately with quartz and other non-clay minerals. Of these kaolinite is the most common one. Its chemical formula is $Al_2O_3.2SiO_2.2H_2O$. China clay is almost pure kaolinite. Clays consist of very small crystalline particles and electron microscopy and x-ray diffraction can demonstrate their crystallinity. Clays are all silicate (SiO_4) based. They have silicon network with oxygen and other elements (*Figure* 3). Here silicon is tetrahedrally coordinated and these tetrahedra form the skeletal network. In kaolinite, the clay minerals are made up of silicon-oxygen sheets and aluminum-hydroxyl sheets. The silicon ions are at the center of a tetrahedron of oxygen ions. The oxygen ions are common to adjacent tetrahedra. The aluminum is at the center of six hydroxyls occupying positions at corners of a regular octahedron. In montmorillonite $[(OH)_2Al_2(Si_2O_5)_2.nH_2O]$, one aluminum-hydroxyl layer is between two silicon-oxygen layers and has two layers of water molecules between these units. Aluminum may also be replaced by magnesium and iron ions in some cases. Illite $[(OH)_4K_x(Al_4Fe_4Mg_{10})(Si_{8-x}Al_x)O_{20}]$ is similar to montmorillonite except that it has no water layers but contains an alkali ion instead.

When clay is mixed with water, it acquires a pasty consistency and in this plastic state very small forces can deform it to make

[6] Vitrification is the process of glass formation.

articles of any shape. When a clay article is dried, it is rigid but fragile. Firing these articles at high temperatures renders them hard and durable. In kaolinite type of clay, at temperatures in the range of 450-600°C, water molecules are driven away and there is a chemical decomposition with the formation of Al_2O_3 and SiO_2. Clay articles finally develop the strength only above 900°C where vitrification[6] occurs. During vitrification the porosity of the mass of clay decreases and its strength and hardness increase.

Clays consist of clay minerals together with varying proportions of other naturally occurring mineral substances, which lend their unique characteristics. Thus, the pleasant red color of terra-cotta (because of some iron compounds), the imperviousness of stoneware and its resistance to corrosion, the delicate translucency of chinaware and porcelain, the high resistance to crushing of some engineering bricks and the extraordinary electrical resistance of insulators are all due to the presence of a suitable proportion of certain elements or compounds which impart their valuable characteristics to these materials. The amount of allowable impurities depends on the purpose for which it is used. For example, clay that has to be used as a refractory material should not contain any alkali, as they will form fluxes with Al_2O_3 and SiO_2 decreasing the high temperature toughness. For the manufacture of white-ware, the clay must not contain coloring impurities, such as iron oxides. Addition of alumina is found to reduce the plasticity of the clay and increase its high temperature toughness.

The structural clay products which are being used include acid-resisting bricks, tiles, tanks and pipes used in the chemical industries and to some extent in others, such as leather manufacture, and in a variety of articles used for power transmission such as cable conduits and insulators. Clay products for the retaining or exclusion of heat at low or moderate temperatures are also included. As far as refractories[7] are concerned, fire-bricks have been in use since about 2000 BC For the past 200 years, silica bricks made of ganister (SiO_2 mineral) and other

[7] A material is called a refractory if it can stand up to the action of corrosive solids, liquids, or gases at high temperatures.

silica rocks were found to be suitable for furnaces used in steel-making. More recently, basic materials such as alumina (Al_2O_3), mullite (Al_2O_3-SiO_2), magnesite ($MgCO_3$), dolomite ($CaCO_3$-$MgCO_3$) and magnesite-chromite (Cr_2O_3-MgO) have been introduced. The choice of refractory material for a given application is determined by the type of furnace or heating unit, and the conditions prevailing like the gaseous atmosphere, the kinds of slags, the type of metal charge and the degree of purity required in the final product. Other properties that may be important for certain applications include electrical conductivity, gas permeability, external appearance and structure. In the processing of metals, cements, glass and other materials, the furnace charge usually reacts physically and chemically with the refractory lining and hence the degree of this reaction governs the life of the lining. In addition to furnace lining, some refractory materials like zirconia (from zircon, $ZrSiO_4$) and graphite (from coke) are used to make crucibles for melting metals.

Even in modern times, many clay-based articles are being used like the tableware, sanitary ware, stoneware and electrical insulation (porcelain for insulators, switch-base, spark plugs and frames for electrical heating appliances).

Glasses

Man from very early times, for which there is archaeological evidence, has used natural glasses. Articles dating back to 2000 BC have been found in Egypt. Beads made from pottery glaze belonging to about 1600 BC have also been excavated. Drinking glasses of 54 AD and window glass of 422 AD belonging to Romans have been found. The first use of glass was for decorative purposes. Then glass was used for containers, which even now is one of the most important uses of glass.

Glass articles are made from molten or semi-molten glass by moulding or blowing. Heating is not the last part of the manufacturing process, as it is with clay products. Many kinds of

Figure 4. Porcelain articles sold on the roadside.

glasses are formed during annealing of ceramics. Thus, glasses are closely linked with ceramics, even the advanced ceramics.

Glass is an amorphous solid, which implies it has no long-range order[8]. Substances in glassy state are not in thermodynamic equilibrium, in contrast to the crystalline state. Traditional glasses have been made of inorganic materials such as silica sand, sodium and potassium carbonates, feldspar, borates, and phosphates that react to form metallic oxides in the final glass. The traditional silicate glasses are still used for making glass containers, windowpanes and automobile windshields.

[8] There is no regularity in the arrangement of its molecular constituents on a scale larger than a few times the size of these constituents.

Making pots of different shapes from clays is a highly skilled job. Clays found in different parts of the world have different colours depending on the minerals that are present. Similarly, making porcelain articles in different shapes and painting them is a large business around the world. Beautifully painted porcelain articles that are sold on roadsides make a colourful sight (*Figure* 4). Glass blowing is another skilled job, which requires tremendous amount of practice to get perfect shapes. Art works made of ceramic materials can be both exquisite and expensive. Thus, even today traditional ceramics find a place all over the world both as utility items and as works of art. In the next part of this article we will look at how these traditional materials are processed and refined to obtain the advanced ceramics.

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