



P O L I T E C H N I K A   Ś L Ą S K A

WYDZIAŁ BUDOWNICTWA

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# ADVANCED CERAMIC IN STRUCTURAL ENGINEERING

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# Advanced Ceramic in Structural Engineering

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# 1.- INTRODUCTION

## 1.1- AIM AND REASON OF THE WORK

The work deals with "Advanced Ceramics in Structural Engineering". Throughout this work we present the different types of ceramic that are currently in wider use, and the main research lines that are being followed.

Ceramics have very interesting properties, both mechanical and electrical and refractory where we can find some of the most interesting points of inquiry. Through this work we try to understand this complex world, analyzing both general and specific properties of different types of advanced ceramics. It also discusses the advantages and disadvantages of their use compared to other materials, and we will make some conclusions about all the work.

## 1.2- HISTORY OF THE CERAMICS

The term ceramics is derived from the greek word "keramas" which means potter's clay. Its origin is a sanskrit term meaning to burn.

Ceramics materials group a great number of inorganic materials, non-metallic or polymers, with different properties and applications. Its history is linked to the history of people all over the world and all over the time.

Ceramics appears for the first time in the Neolithic. It is one of the most ancient industries on the planet. It was born when humans discovered that clay could be dug up and formed into objects by first mixing with water and then firing. As early as 24000 B.C., animal and human figures were made from clay and other materials and were fired in kilns partially dug into the ground.

Almost 10000 years later, as settled communities were established, tiles were manufactured in Mesopotamia and India. The first use of functional pottery vessels for storing water and food is thought to be around 6000 or 10000 B.C. clay bricks were also made around the same time.

Glass was believed to be discovered in Egypt around 8000 B.C., when overheating of kilns produced a colored glaze on the pottery. Experts estimate that it was not until 1500 B.C. that glass was produced independently of ceramics.

Fast forward to the Middle Ages, when the metal industry was in its infancy. Furnaces at that time for melting the metal were constructed of natural materials when synthetic materials with better resistance to high temperatures (called refractories) were developed.

In the 16th century, the industrial revolution was born. These refractories created the necessary conditions for melting metals and glass on an industrial scale, as well as for the manufacture of, cement, chemicals and ceramics.

In the 19th century, with the invention of the electric light by Thomas Alva Edison and the telephone by Alexander Graham Bell, a new era which could be referred to as the “era of electricity” began. Ceramics, previously used only as vessels, started to play entirely new roles suited to this area and material for electrical insulation were developed.

The 20th century brought the advent of electronics, with the start of radio and television broadcasts and the invention of the transistor. This era was facilitated by ceramics from the beginning, when large vacuum tubes of the early 20th century relied on ceramics materials. Within wireless equipment, only ceramics possessed the properties necessary to provide high signal output even over high frequency ranges. Ceramics could not be replaced with other materials.

Ceramics materials are nowadays widely used in many fields of technology like electronics, aeronautics, aerospace, medicine, food and Chemicals industries... Ceramics as material has been continually evolved to make sure that in nowadays world, it is environment friendly and can be easily disposed off also. These materials are hard and hence pose challenges when they are recycled as they cannot break down easily. So there is more research being done nowadays to look into this aspect of the ceramics.

### 1.3.- DIFFERENT KINDS OF CERAMICS

The ceramics are basically divided into three groups:

- Amorphous ceramics: they are the glasses.  
Based on silica,  $\text{SiO}_2$  + additives to decrease the melting temperature.
- Traditional ceramics: products made of clay, silica and feldspar.  
Clay:  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 6\text{SiO}_2$   
Silica:  $\text{SiO}_2$   
Feldspar:  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ 
  - Porous ceramics (bricks, pottery, earthenware)
  - Compact ceramic (porcelain, stoneware)
  - Refractory ceramic (porcelain for thermal insulation)
- Advanced ceramics:
  - Refractory ceramics
  - Piezoelectrics and ferroelectrics
  - Electro-optical
  - Abrasive ceramics: nitrides and carbides
  - Superconductor ceramics
  - Biocompatible ceramics: hydroxyapatite

## 2.- STRUCTURE AND DEFECTS

The properties of ceramic materials are mainly influenced by the type of structure that they have, throughout this chapter there will be an overview of the main structures and their influence on the properties of ceramics that have this structure.

Ceramic materials can have the following structures: crystalline, amorphous or mixed.

### 2.1 STRUCTURE OF CERAMIC MATERIAL

#### 2.1.1 CERAMIC BOND

The ceramic materials can be crystalline, amorphous or mixture of both

Percentage of ionic and covalent character of the bond for some ceramic materials, it determines the crystalline structure.

Using Pauling's formula you can determine the percentage of ionic character of a reaction:

$$Pauling : \% \text{ Ionic character} = 100 \cdot \left\{ 1 - e^{\frac{-(\chi_A - \chi_B)^2}{4}} \right\}$$

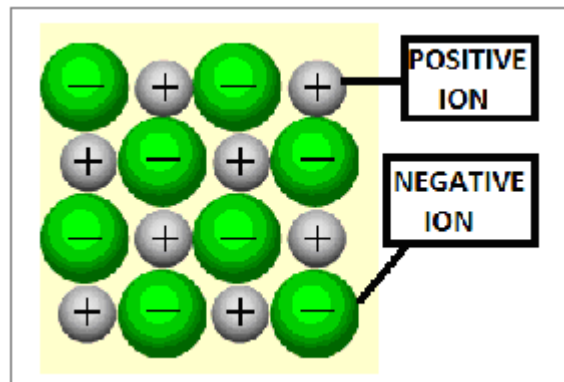
We can see the percentage of ionic character for some ceramic materials:

Material	$\chi_A$	$\chi_B$	$[(\chi_A - \chi_B)/2]^2$	$C_C$	$C_I$
Vc	1,5	2,5	0,25	0,446	0,221
NbC	1,3	2,5	0,36	0,365	0,302
TiC	1,3	2,5	0,36	0,365	0,302
VN	1,5	3,1	0,64	0,527	0,473
NbN	1,3	3,1	0,81	0,445	0,555
TiN	1,3	3,1	0,81	0,445	0,555

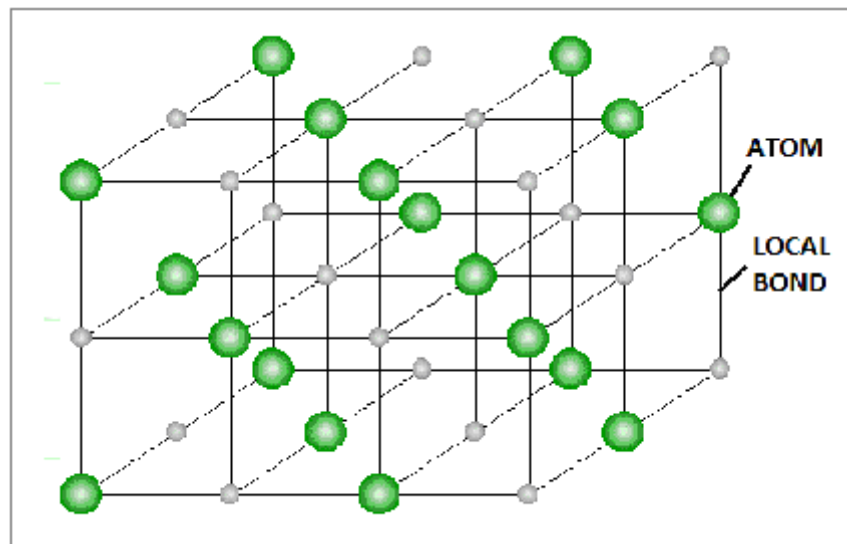
To see the difference between the different types of bonds, below all these types are shown, the ionic, the covalent and metallic:



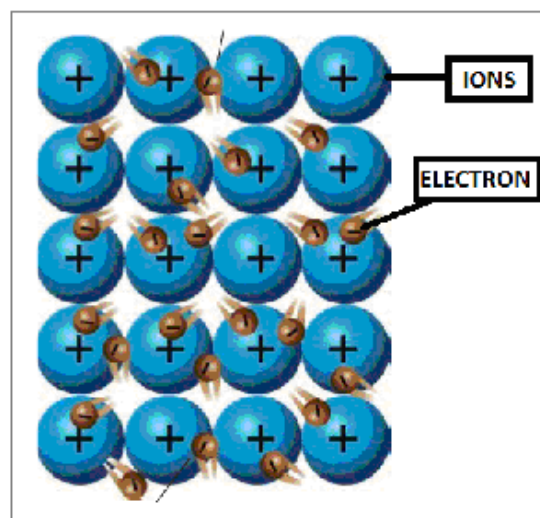
- Ionic bond:



- Covalente bond:



- Metallic bond:



### 2.1.2 PACKING OF IONS IN CRYSTAL STRUCTURES

This is something that happens in the ionic structures, the packing of anions with cations in interstices. The ions tend to pack densely in order to reduce  $E_{\text{total}}$ .

The factors that determine the packaging are:

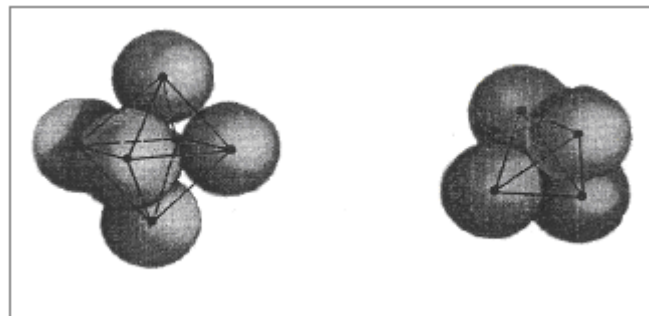
- Sizes  $C^+A^-$ , es decir,  $r_{\text{cation}} < r_{\text{anion}}$
- Electroneutrality
- Coordination Index, by increasing C.I.  $\Rightarrow$  increase stability
- Sharing of polyhedral: sharing vertices instead of edges or faces, increases the distance between cations.

Interstitial positions in compact networks can be:

- Tetrahedral
- Octahedral

Depending on the number of atoms per cell ( $n$ ) in fcc structures (face centered cubic) and h.c.p. (hexagonal close packed) you can determine the number of interstitial positions that may be occupied.  $2n$  for tetrahedral and  $n$  for octahedral.

By the next picture you can see better the octahedral and tetrahedral positions:



The interstitial positions are very important, because in the next section we will see that depending on which occupies will form a different structure, completely changing the properties of the material.

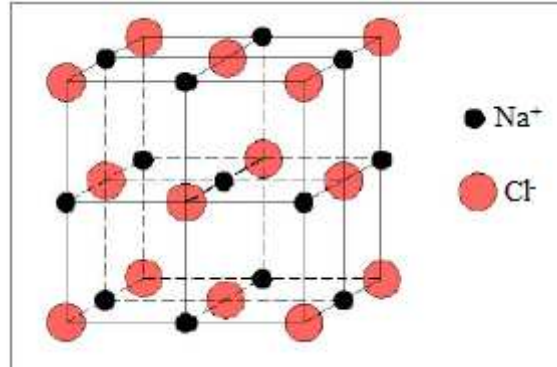
In the case of the left is an octahedral interstitial position formed in the center, where six atoms touch each other. In the second case, tetrahedral interstitial position formed in the center, where four atoms touch each other.

The interstitial positions are very important, because in the next section we will see that definitive structure depends on which interstitial position is occupied, changing the properties of the material.

### 2.1.3 CRYSTAL STRUCTURES

There are many crystal structures in this section we will see the main ones:

- **Crystal structure type NaCl**



$\text{Cl}^-$ : FCC packing

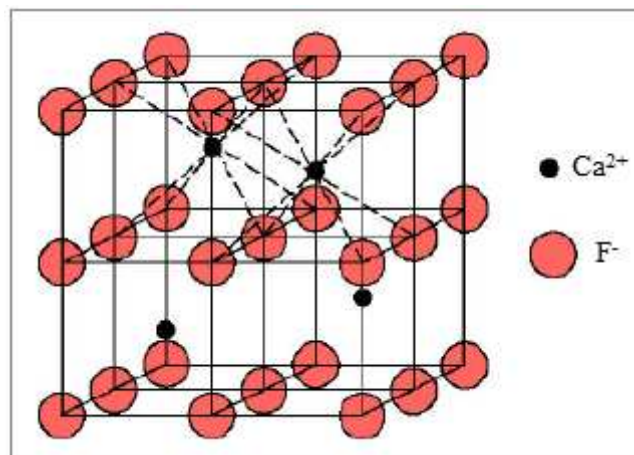
$\text{Na}^+$ : all octahedral interstitials

4  $\text{Na}^+$  and 4  $\text{Cl}^-$  per unit cell

C.I.=6

Ceramics that have this type of structure:  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{FeO}$ ,  $\text{NiO}$

- **Crystal structure type fluorite ( $\text{CaF}_2$ )**



$\text{Ca}^{2+}$ : FCC packing

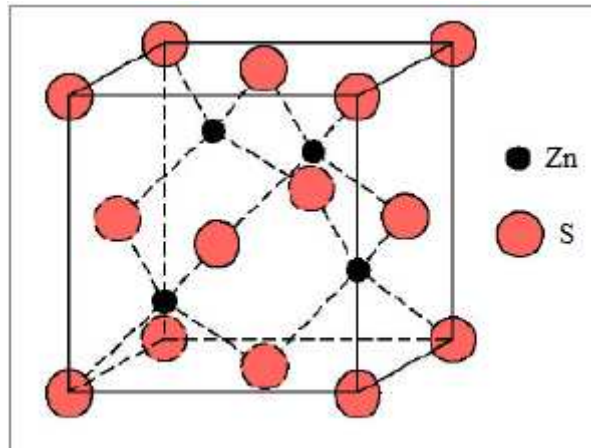
$\text{F}^-$ : all tetrahedral interstitials

I.C. ( $\text{Ca}^{2+}$ ): 8

I.C. ( $\text{F}^-$ ): 4

Ceramics that have this type of structure:  $\text{UO}_2$ ,  $\text{ThO}_2$ ,  $\text{ZrO}_2$

- **Crystal structure type blende (ZnS)**



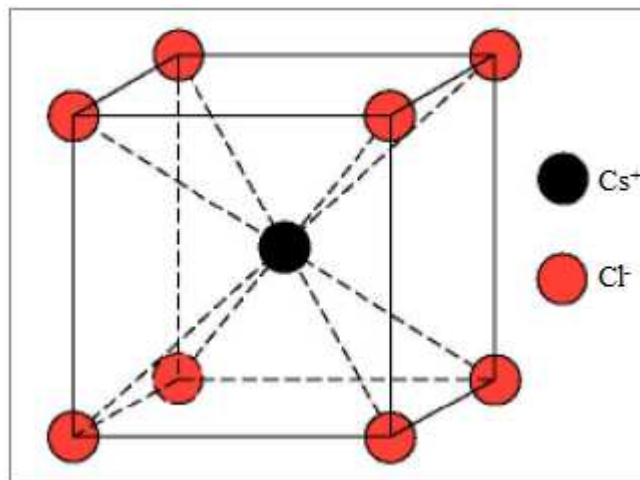
$S^{2-}$ : FCC packing

$Zn^{2+}$ :  $\frac{1}{2}$  tetrahedral interstitials

4  $Zn^{2+}$  and 4  $S^{2-}$  per unit cell

Ceramics that have this type of structure: Typical semiconductors: GaAs, InP, InSb

- **Crystal structure type CsCl**



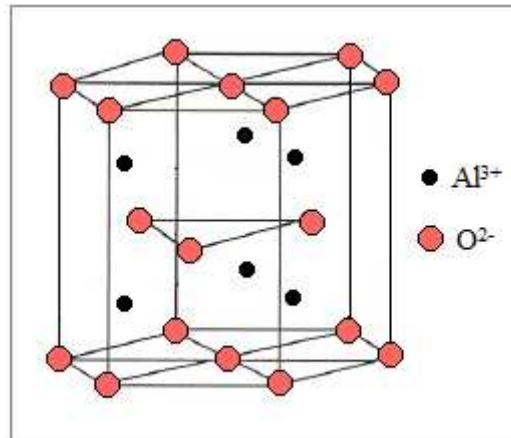
$Cl^-$ : BCC packing

$Cs^+$ : centre of the cube

C.I.: 8

Ceramics that have this type of structure: CsBr, TlCl, TlBr

- **Crystal structure type Corundum (Alumina)**



$O^{2-}$ : HCP packing (6 ions)

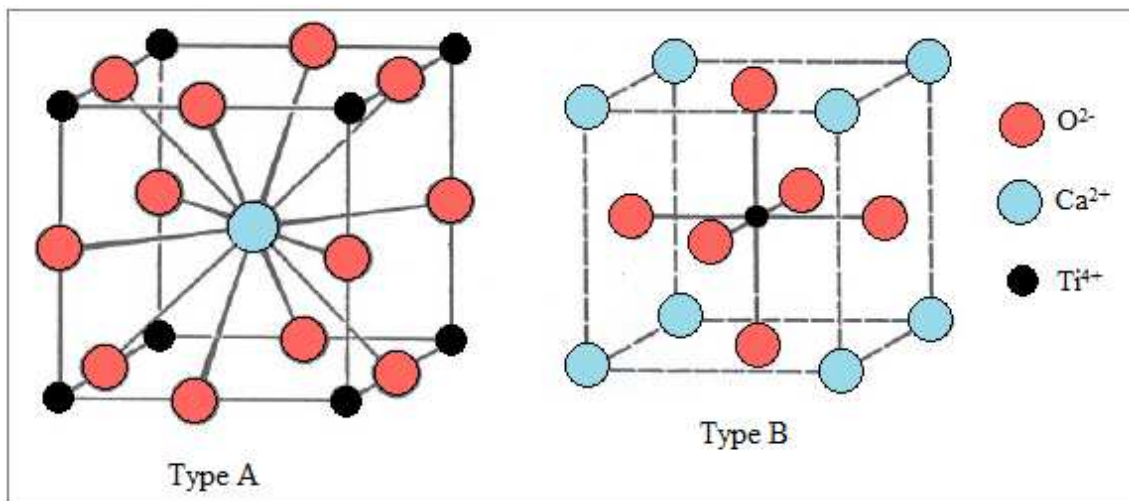
$Al^{3+}$ :  $2/3$  octahedral interstitials (4 ions)

I.C.( $Al^{3+}$ ): 6

I.C.( $O^{2-}$ ): 6

Ceramics that have this type of structure:  $Cr_2O_3$ ,  $FeO_3$ ,  $Al_2O_3$

- **Crystal structure type Perovskite  $ABO_3$**



$O^{2-}$  and  $Ca^{2+}$ : FCC packing

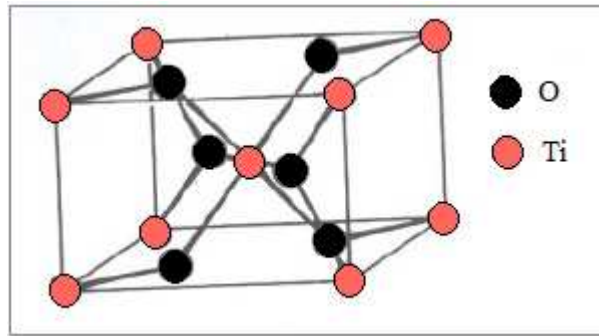
$Ti^{4+}$ :  $1/4$  octahedral interstitials

C.I.( $Ti^{4+}$ ): 6

C.I.( $Ca^{2+}$ ): 12

Ceramics that adopt this type of structure:  $BaTiO_3$ ,  $CaZrO_3$ ,  $SrTiO_3$  (electroceramics applications: ferroelectric, piezoelectric, ...)

- **Crystal structure type Rutile:  $\text{TiO}_2$**



$\text{O}^{2-}$ : HCP packing

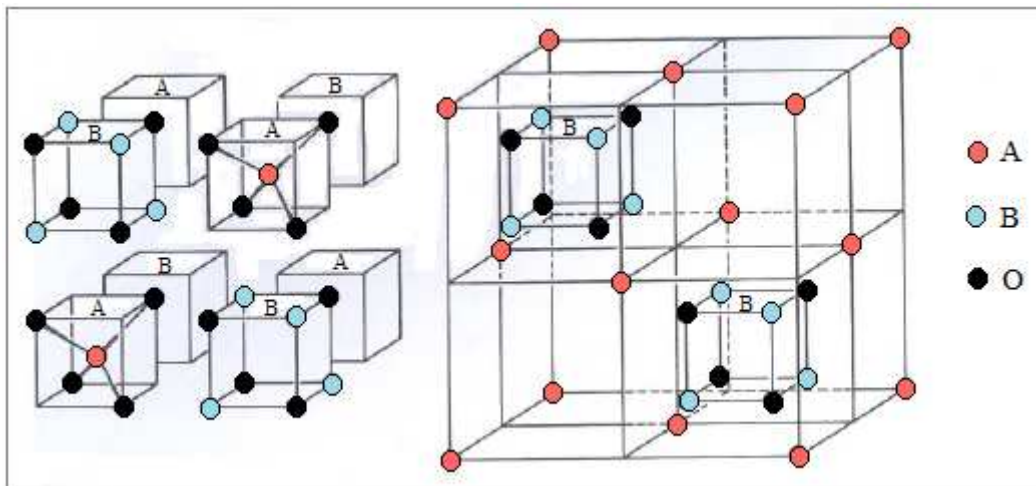
$\text{Ti}^{4+}$ :  $\frac{1}{2}$  tetrahedral interstitials

C.I. (Ti): 6, distorted octahedron

C.I. (O): 3, almost equilateral triangle

This type of ceramics is used as bleaching (paints, plastics) and as electrodes in electrochemical devices

- **Crystal structure type Spinel  $\text{AB}_2\text{O}_4$**



Spinel mineral ( $\text{MgAl}_2\text{O}_4$ )

$\text{O}^{2-}$ : FCC packing

Unit cell of 56 ions (8 A, 16 B and 32 O) and 96 reticular positions

There are 64 tetrahedral interstitials, occupied  $\frac{1}{8}$ , thus: 8 tetrahedral interstitials.

There are 32 octahedral interstitials, occupied  $\frac{1}{2}$ , therefore: 16 octahedral interstitials.

Normal spinel:

$\text{A}^{2+}$ : 8 tetrahedral interstitials

$\text{B}^{3+}$ : 16 octahedral interstitials

Inverse spinel:

$\text{A}^{2+}$ : 8 octahedral interstitials

$\text{B}^{3+}$ : 8 octahedral interstitials

$\text{B}^{3+}$ : 8 tetrahedral interstitials

Commercial magnetic ceramics are based on spinel structure:  $\text{MgFe}_2\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$ ,  $\text{MnFe}_2\text{O}_4$  and other oxides ferrimagnetic.  
They are transformer cores, read-write heads for magnetic data storage...

#### 2.1.4 COVALENT CERAMICS

- **Diamond, structure type blend**

High hardness and abrasive.  
Bond 100% covalent, tetrahedral  $\text{CC}_4$ .

- **SiC, Diamond type structure (spherullite)**

Good abrasive properties, high hardness, chemical inert.  
89% covalent bond.

- **$\text{Si}_3\text{N}_4$ , Cutting elements, blades, rotors**

$\text{SiN}_4$  tetrahedral  
N coordinated to 3 Si  
Open structure, 70% covalent bond.

- **Sialons,  $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$**

It is a solid solution between nitrides and oxides. Derived from  $\text{Si}_3\text{N}_4$ , by substituting z atoms of Si for Al atoms. In order to compensate the valence difference, the same number of N atoms are substituted by O. Cutting tools, antifriction rollers, motors components.

#### 2.2 DEFECTS

Defects are a property of solids, there are "n" flaws or defects.

Perfect crystals:

- All atoms are in ideal lattice positions (only at 0 K)

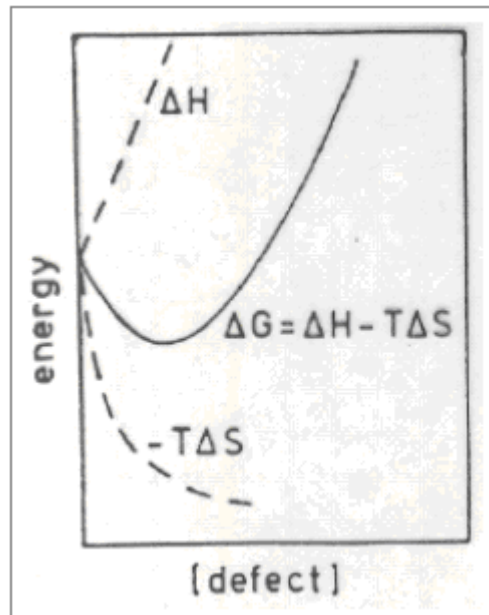
Real crystal:

- The atoms are vibrating in their atomic positions
- There are unoccupied positions (vacancies)
- The atoms are displaced from their ideal atomic positions

So there are "n" defects that alter the properties and the structural regularity of the material.

The thermodynamic justifies the existence of defects, which decrease the free energy ( $\Delta G_{\text{crystal}}$ )

$$\Delta G_{\text{crystal}} = \Delta H - T\Delta S$$



- When the number of defects increases  $\Rightarrow \downarrow \Delta S \Rightarrow \Delta H$  can be  $\geq \Delta S \Rightarrow \Delta G > 0$
- There is an optimum number of defects for all crystals have defects
- When the temperature increases  $\Rightarrow \uparrow$  [defects]

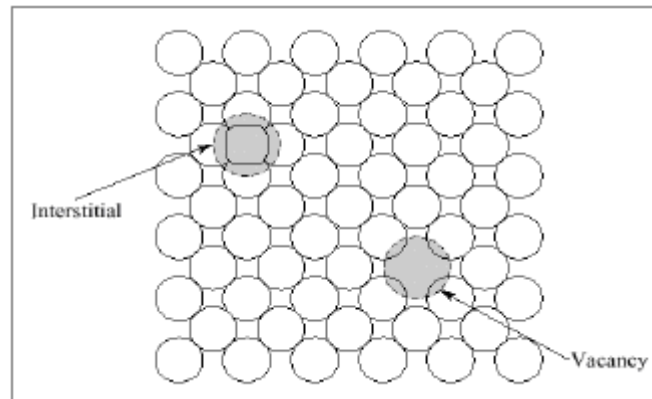
There are different types of defects depending on their size:

- Point defects:
  - Vacancy
  - Interstitial
  - Schottky
  - Frenkel
  - Antisite defects
  - Color centers
- Line defects:
  - Edge dislocations
  - Screw dislocations
  - Mixed dislocations
- Planar defects:
  - Surface
  - Grain boundaries
  - Twin plane
  - Stacking faults

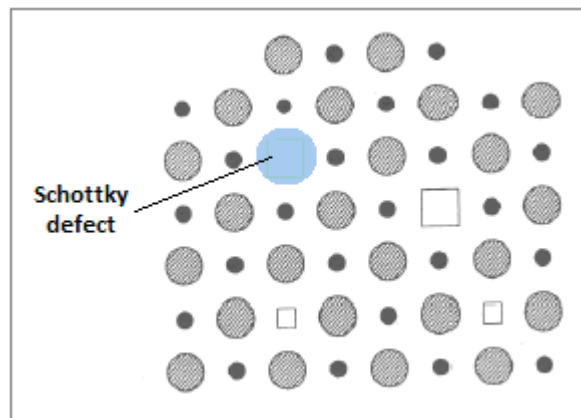


### 2.2.1 POINT DEFECTS

- **Vacancy**: they are lattice sites which would be occupied in a perfect crystal, but are vacant.
- **Interstitial**: are atoms that occupy a site in the crystal structure at which there is usually not an atom (less abundant than vacancies).



- **Schottky defect**: vacancy in an ionic crystal.



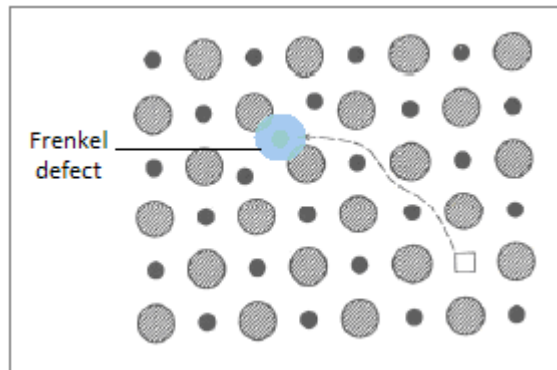
The concentration of these defects is measured with the following formula:

$$n_s = N \exp \left[ -\frac{\Delta H_s}{2kT} \right]$$

$\Delta H_s$ : Eg Schottky defects creation

N: number of lattice positions

- **Frenkel defect**: is the movement of an ion from its normal position to an interstitial position.



The concentration of these defects is measured with the following formula:

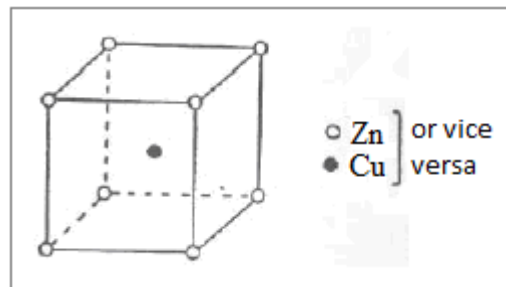
$$n_F = (N \times N_i)^{\frac{1}{2}} \exp\left[-\frac{\Delta H_F}{2kT}\right] [\text{n}^\circ/\text{m}^3]$$

$\Delta H_F$ : Eg Frenkel defects creation

$N_i$ : number of interstitial positions

- **Antisite defects**: occur when atoms of different type exchange positions.

This is an order-disorder phenomenon. At low temperature is an "orderly" structure, while at high temperatures we find a "disorderly" structure. As in the example below:



The degree of disorder is a function of temperature, so the total disorder is reached at the critical temperature.

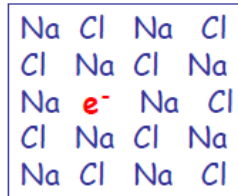
- **Color center**: unpaired electrons trapped in anionic vacancies positions in the network.

It is produced by:

- Irradiation of intense light (X-ray, UV, neutrons, ...)
- Heating in the vapour of the metal

Vapor atoms diffuse into the crystal and are located in cationic positions, while creating an equivalent number of anionic vacancies, and ionization produces an alkali metal cation with an electron trapped in the anion vacancy.

The electron trapped behaves like a particle in a potential box with only certain levels possible  $E_g$ , where  $E_g$  is in contrast to the visible part of electromagnetic spectrum (F center or "Farbenzentre").



Therefore materials doped with certain elements can be achieved one color or another.

### 2.2.2 LINE DEFECTS

They are called dislocations: Defects that lead to a distortion of the network centred around a line.

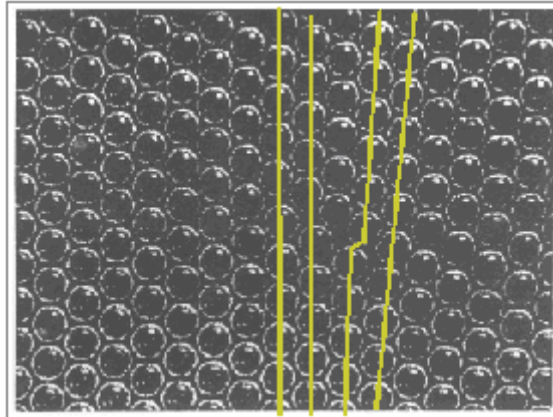
Formation:

- During the solidification
- For permanent or plastic deformation of the crystal
- By condensation of vacancies
- For atomic distortions in solid solutions.

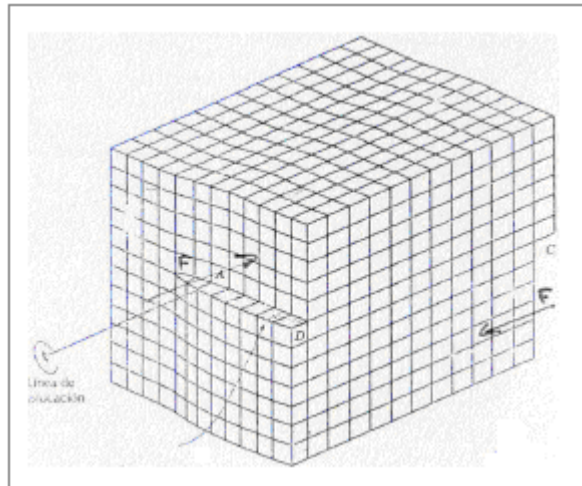
Types:

- Edge dislocations
- Screw dislocations
- Mixed dislocations

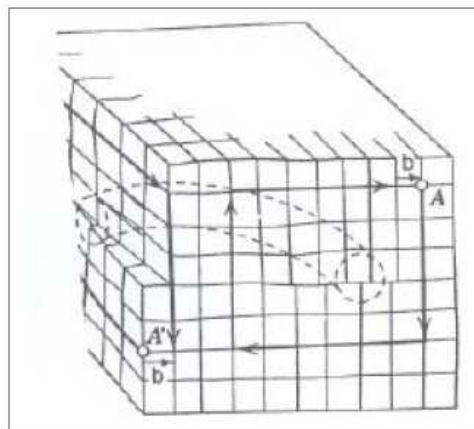
- **Edge dislocations**: is a defect where an extra half-plane of atoms is introduced mid way through the crystal, distorting nearby planes of atoms.



- **Screw dislocations**: are due to shear stress, is a spiral-shaped distortion.



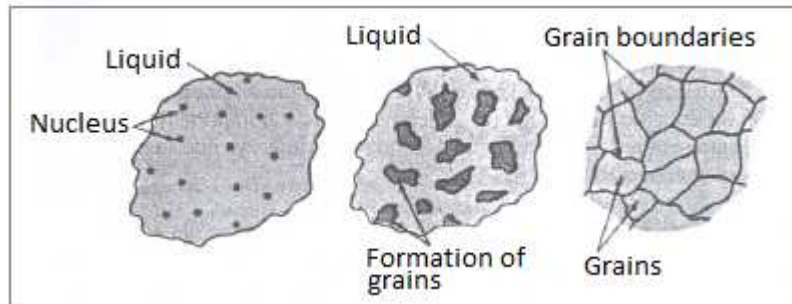
- **Mixed dislocations**: is a combination of the previous, end on the surface, never within the crystal.



### 2.2.3 PLANAR DEFECTS

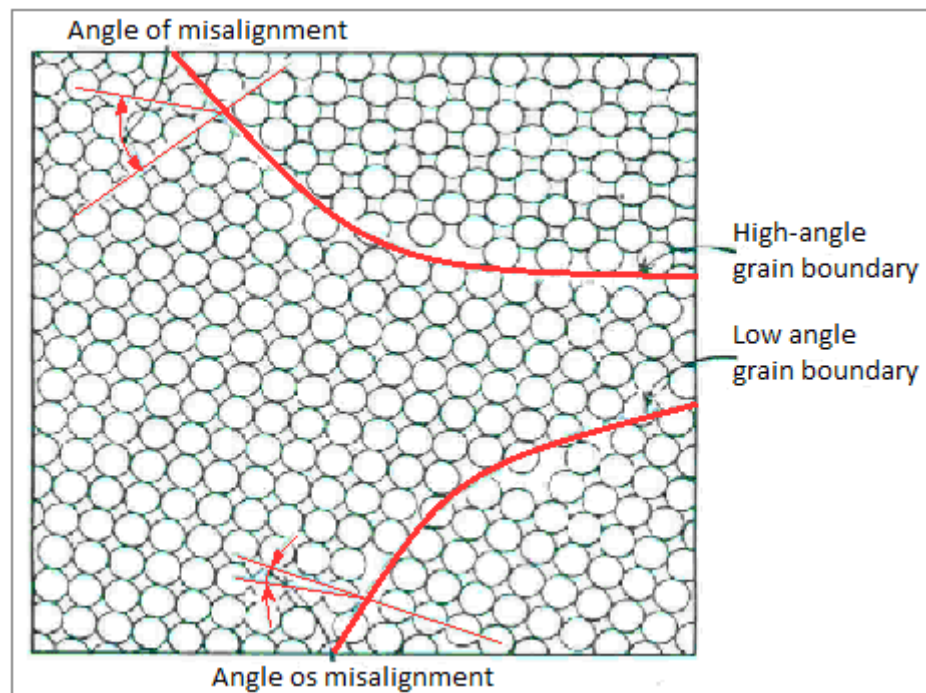
- **Grain boundaries:** Interface between two crystals with different orientation. The thickness =  $f$  (Temp. Sintering, time, atmosphere, atomic mobility, ...)

Formation: During the solidification process are formed different crystals from different nucleus that grow simultaneously.



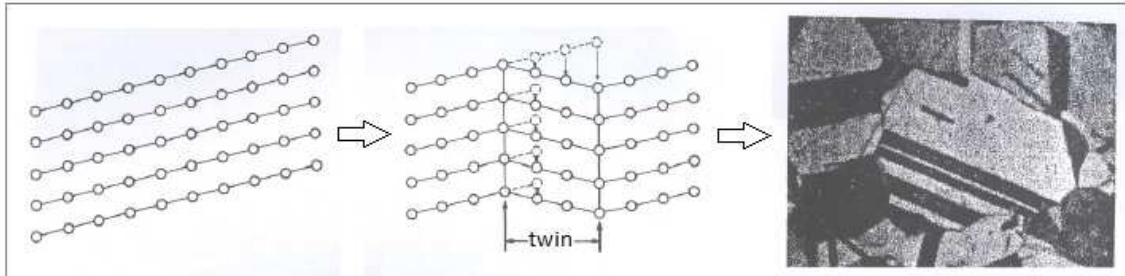
Clasification of grain boundaries:

- High-angle grain boundary (orientation difference greater than  $15-20^\circ$ )
- Low-angle grain boundary



- **Twin planes**: Plane that separates two parts of a grain with a small difference in the orientation of their planes (twins = plane of reflection)

Formation: Processes of deformation or heat treatment.



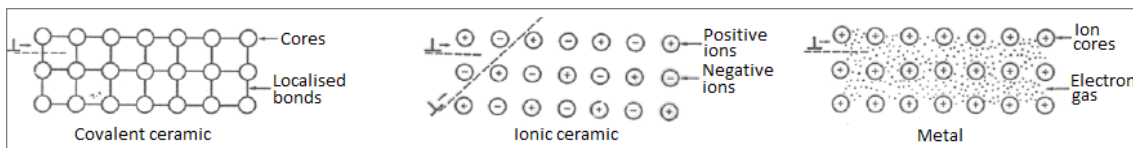
## 3.- MECHANICAL PROPERTIES

### 3.1 HARDNESS

Hardness is the measure of how resistant solid matter is to various kinds of permanent shape change when a force is applied.

Ceramics are very hard solids, more than metallic materials, this is because their ionic or covalent bonds are stronger than metal bonds:

$\text{Hardness}_{\text{Covalents}} (\text{diamond, SiC}) > \text{Hardness}_{\text{ionics}} (\text{Al}_2\text{O}_3, \text{ZrO}_2) > \text{Hardness}_{\text{metallics}}$



The hardness of ceramic materials is a property which is of high significance as it relates to the ability of the material to withstand penetration of the surface through a combination of brittle fracture and plastic flow.

Often, hardness is directly equated to wear resistance. This is a mistaken concept with many metallic components and is definitely an incorrect selection criterion with regards to engineering ceramic materials.

Wear behaviour of ceramic materials is complex and is dependent upon many variables, of which hardness is an important variable but not the only significant variable.

For example, in many wear environments, such as the erosive wear behaviour of oxide engineering ceramics, it is the ratio of fracture toughness to hardness which is found to be of most significance in determining the wear performance.

In many wear environments, a much softer material such as a zirconia can outperform harder materials such as alumina or silicon carbide.

Hardness measurements in engineering ceramics are generally measured using a Vickers hardness test. In this test a pyramidal diamond indenter is pressed into a polished surface under known loading conditions and the size of the indentation is related to the hardness of the material.



Vickers hardness tester



Rockwell hardness tester

It should also be noted that the hardness value quoted for any material is a function of the type of test conducted and the loading conditions employed. Lighter loads typically provide higher hardness values.

Other factors that need to be taken into account when interpreting hardness data for ceramic materials are the amount of porosity in the surface, the grain size of the microstructure and the effects of grain boundary phases.

Some typical hardness values for ceramic materials are:

Material Class	Vickers Hardness (HV) GPa
Glasses	5 – 10
Zirconias, Aluminium Nitrides	10 - 14
Aluminas, Silicon Nitrides	15 - 20
Silicon Carbides, Boron Carbides	20 - 30
Cubic Boron Nitride CBN	40 - 50
Diamond	60 – 70 >

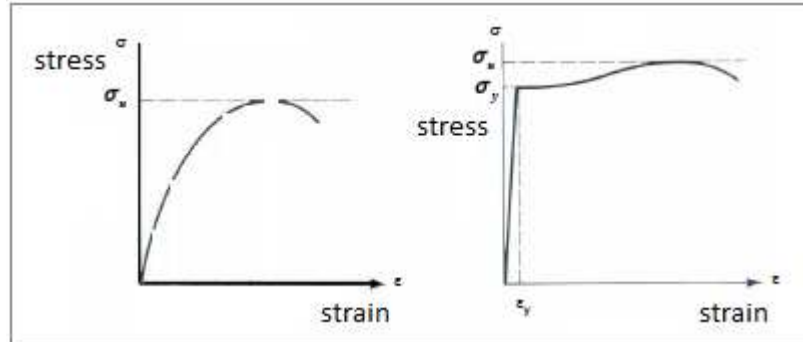
### 3.2 YOUNG'S MODULUS

Young's modulus, also known as the tensile modulus, is a measure of the stiffness of an elastic material and is a quantity used to characterize materials. It is defined as the ratio of the uniaxial stress over the uniaxial strain in the range of stress in which Hooke's Law holds. It can be experimentally determined from the slope of a stress-strain curve created during tensile tests conducted on a sample of the material.

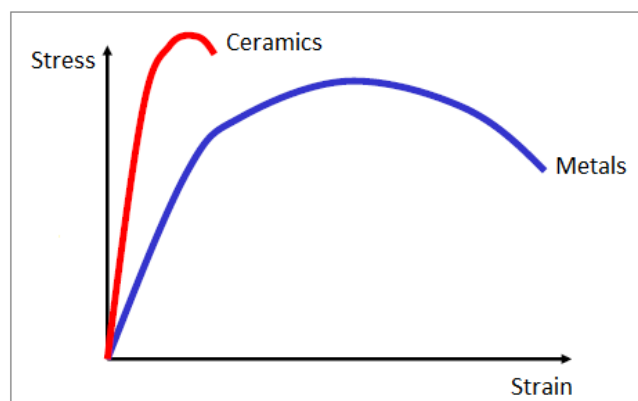


In anisotropic materials, Young's modulus may have different values depending on the direction of the applied force with respect to the material's structure.

The stress-strain curve can present the following ways:



Comparing ceramic materials with metals the curves have the following form:



For some materials are observed, in this curve, a first tranche in which the relationship between stress and deformation is linear, being fulfilled:

$\sigma = E\epsilon$ , equation known as Hooke's law.

Where  $E$  is called Young's modulus and is an intrinsic property of the material, by what it is not function of time of load application, and takes very different values if is a material or if is another.

For the case of ceramic materials, they possess a greater  $E$  due to the type of bond ( $E_{\text{ceramics}} > E_{\text{metallics}}$ ). Ceramics also have a low density, which leads to having high  $E_{\text{specific}}$ . Due to these properties are widely used as fibers in composite materials.

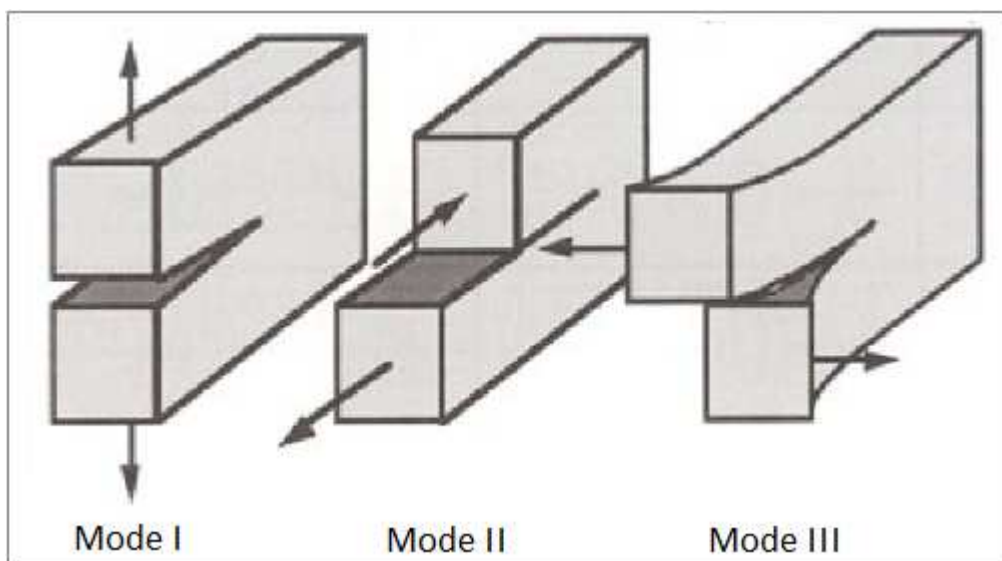
Below are the values for different materials:

Material	Modulus E (GPa)	Density ( $\text{mg}\cdot\text{m}^{-3}$ )	Specific modulus ( $E/\rho$ )
Steels	210	7.8	27
Al Alloys	70	2.7	26
Alumina, $\text{Al}_2\text{O}_3$	390	3.9	100
Silica, $\text{SiO}_2$	69	2.6	27
Cement	45	2.4	19

### 3.3 FRACTURE TOUGHNESS

Fracture toughness is an indication of the amount of stress required to propagate a preexisting flaw. It is a very important material property since the occurrence of flaws is not completely avoidable in the processing, fabrication, or service of a material/component. Flaws may appear as cracks, voids, metallurgical inclusions, weld defects, design discontinuities, or some combination thereof. Since engineers can never be totally sure that a material is flaw free, it is common practice to assume that a flaw of some chosen size will be present in some number of components and use the linear elastic fracture mechanics (LEFM) approach to design critical components. This approach uses the flaw size and features, component geometry, loading conditions and the material property called fracture toughness to evaluate the ability of a component containing a flaw to resist fracture.

A parameter called the stress-intensity factor (K) is used to determine the fracture toughness of most materials. A Roman numeral subscript indicates the mode of fracture, there are three modes of fracture. Mode I fracture is the condition in which the crack plane is normal to the direction of largest tensile loading. This is the most commonly encountered mode and, therefore, for the remainder of the material we will consider  $K_I$ .



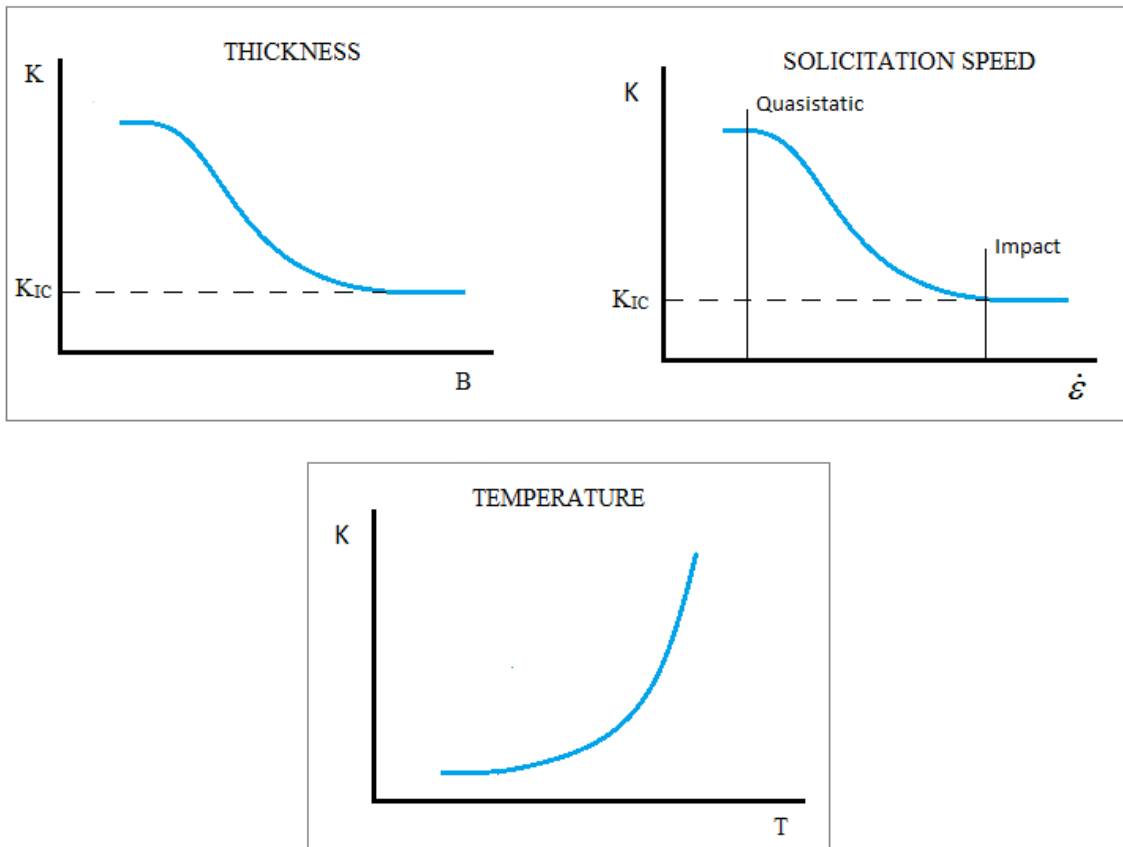
The stress intensity factor is a function of loading, crack size, and structural geometry. The stress intensity factor may be represented by the following equation:

$$K_I = \beta \sigma \sqrt{\pi \cdot a}$$

Where:

- $K_{IC}$  is the fracture toughness
- $\sigma$ , is the applied stress
- $a$ , is the crack length
- $\beta$ , is a crack length and component geometry that is different for each specimen and is dimensionless

There influence of different factors: this factors are the thickness, the temperature and the solicitation speed.



For example in the case of thickness, specimens having standard proportions but different absolute size produce different values for  $K_I$ . This results because the stress states adjacent to the flaw changes with the specimen thickness ( $B$ ) until the thickness exceeds some critical dimension. Once the thickness exceeds the critical dimension, the value of  $K_I$  becomes relatively constant and this value,  $K_{IC}$ , is a true material property which is called the fracture toughness. The stress intensity,  $K_I$ , represents the level of “stress” at the tip of the crack and the fracture toughness,  $K_{IC}$ , is the highest value of stress intensity that a material under very specific (plane-strain) conditions that a material can withstand without fracture. As the stress intensity factor reaches the  $K_{IC}$  value, unstable fracture occurs.

The ceramic is characterized by low KIC. The fracture occurs due to the high number of defects that act as stress concentrator, when dealing ceramics have low plastic deformation, so the crack propagates to cause brittle fracture and catastrophic.

The defects that have a ceramic are:

- Surface cracks
- Pores
- Inclusions
- Grains large

### 3.4 THERMAL SHOCK

Thermal shock is the name given to cracking as a result of rapid temperature change. Ceramics are particularly vulnerable to this form of failure, due to their low toughness, low thermal conductivity, and high thermal expansion coefficients. However, they are used in many high temperature applications due to their high melting point.

Thermal Shock Resistance is an ability of material to withstand sharp changes in temperature.

If a ceramic material is rapidly cooled, its surface reaches the temperature of cooling environment and tends to contract (thermal contraction). Since the interior regions of the material are still hot, thermal contraction of the skin surface is impossible.

This leads to formation of tensile stress in the skin. Such thermal stresses may cause cracks and consequent failure.

Thermal shock resistance of a material may be estimated in accordance to the formula:

$$R_s = \frac{\lambda \cdot \sigma_F}{\alpha \cdot E}$$

Where:

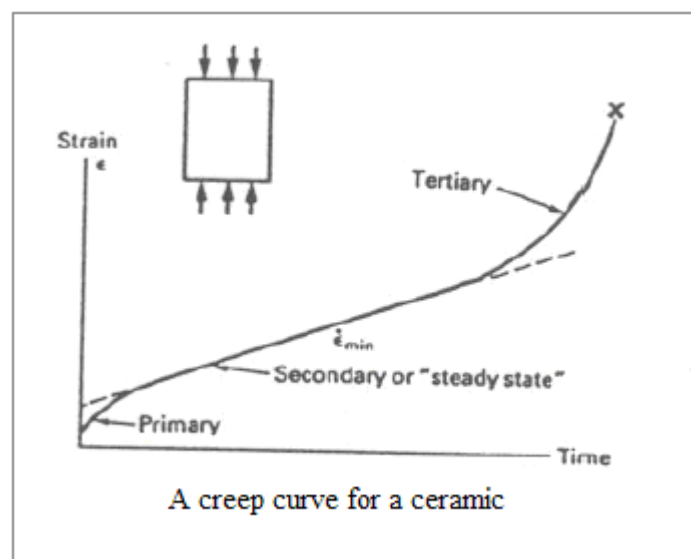
- $R_s$  is the thermal shock resistance
- $\lambda$  is the thermal conductivity
- $\sigma_F$  is the flexural strength
- $\alpha$  is the coefficient of thermal expansion
- $E$  is the modulus of elasticity

### 3.5 CREEP

In materials science, creep is the tendency of a solid material to slowly move or deform permanently under the influence of stresses. It occurs as a result of long term exposure to high levels of stress that are below the yield strength of the material. Creep is more severe in materials that are subjected to heat for long periods, and near melting point. Creep always increases with temperature.

The rate of this deformation is a function of the material properties, exposure time, exposure temperature and the applied structural load. Depending on the magnitude of the applied stress and its duration, the deformation may become so large that a component can no longer perform its function

It is only important in applications of high temperature (refractory)



### 3.6 FLEXURAL STRENGTH

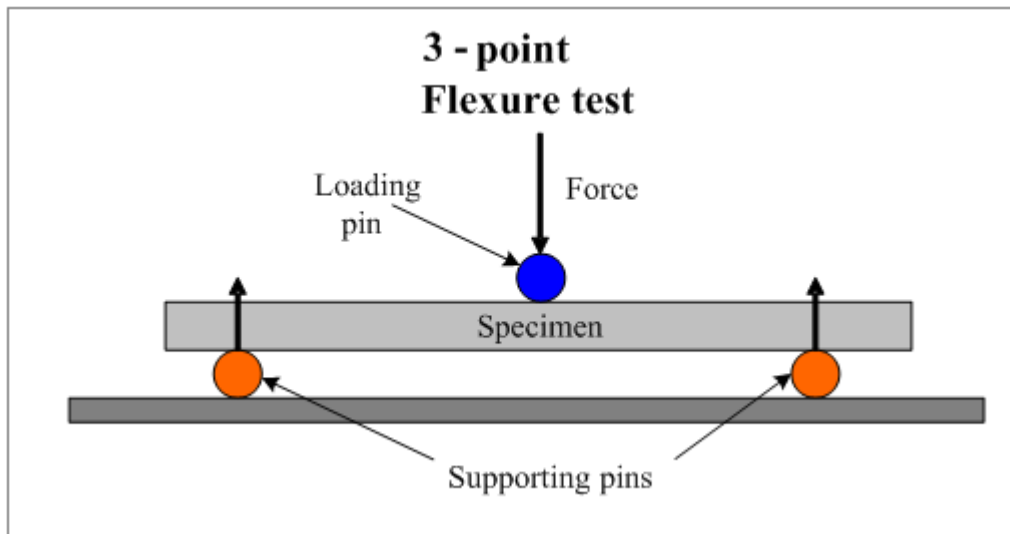
Flexural strength, a mechanical parameter for brittle material, is defined as a material's ability to resist deformation under load. The flexural strength represents the highest stress experienced within the material at its moment of rupture.

Extremely low ductility of ceramic materials does not allow measuring their mechanical properties by conventional tensile test, which is widely used for metals. Brittle Materials, including ceramics, are tested by Flexure Test

There are two standard Flexure Test methods:

- 3 point flexure test
- 4 point flexure test

The most common is 3 point flexural test. In this test a specimen with round, rectangular or flat cross-section is placed on two parallel supporting pins. The loading force is applied in the middle by means loading pin.



### 3.7 WEAR BEHAVIOUR

Wear is erosion of material from its original position on a solid surface performed by the action of another surface.

The wear behaviour of engineering ceramics is relatively complex and is subject to many variables.

Cracking, plastic deformation, tribochemical interaction, abrasion and surface fatigue have all been identified as wear mechanisms operative in ceramic sliding wear situations.

The individual ceramic microstructures also affect the wear behaviour in a fundamental manner.

When one considers the intimate contact of two sliding surfaces where hard particles are either present or formed during sliding, abrasive wear can occur as a consequence of both plastic deformation and fracture mechanisms.

However, in polycrystalline ceramics, the amount of plastic deformation that can occur is strictly limited by the available slip systems and twinning modes. Consequently, abrasive wear is aided by fracture mechanisms initiated by the inelastic structure of the material

### 3.8 ELECTRICAL PROPERTIES

The following electrical properties are characteristic for ceramic materials:

- **Insulating properties**

In contrast to metals, ceramics have very low electrical conductivity due to their ionic and covalent bonding which does not form free electrons.

- **Electrical conductivity**

This is the ability of material to conduct electric current.

The electrical conductivities differ by a factor as large as  $10^{12} \dots 10^{21}$  between metallic and ceramic materials.

Most of ceramic materials are dielectric (materials, having very low electric conductivity, but supporting electrostatic field).

Electrical conductivity of ceramics varies with the frequency of field applied and also with temperature. This is due to the fact that charge transport mechanisms are frequency dependent.

- **Dielectric Strength**

One of most important dielectric properties is Dielectric Strength (ability of a material to prevent electron conductivity at high voltage). Dielectric strength is determined as value of electric field strength (expressed in V/m) at which electron conductivity breakdown occurs.

- **Dielectric Constant**

Other important property of dielectric materials is Dielectric Constant - relative (to vacuum) ability of a material to carry alternating current (dielectric constant of vacuum equals to 1).

Capacitance of a capacitor is directly proportional to the dielectric constant of the dielectric material used in the capacitor.

Dielectric ceramics are used for manufacturing capacitors, insulators and resistors.

- **Semi-conducting properties**

Ceramics based on ZnO may possess semi-conducting properties when they are appropriately doped.

The semi-conducting ceramics are usually prepared by liquid phase sintering with control of grain boundary structure.

Semi-conducting ceramics are used for manufacturing varistors (resistors with non-linear current-voltage characteristic, which are used for over-voltage protection) and Positive Temperature Coefficient (PTC) Resistors.

- **Superconducting properties**

Despite of very low electrical conductivity of most of the ceramic materials, there are ceramics, possessing superconductivity properties (near to zero electric resistivity).

Lanthanum (yttrium), barium or copper oxide ceramic may be superconducting at temperature as high as 138 K. This critical temperature is much higher, than superconductivity critical temperature of other superconductors (up to 30 K).

The critical temperature is also higher than boiling point of liquid Nitrogen (77.4 K), which is very important for practical application of superconducting ceramics, since liquid nitrogen is relatively low cost material.

Such ceramic superconductors are called High Temperature Superconductors (discovered in 1986 by Mueller and Bednorz).

- **Piezoelectric properties**

Piezoelectric effects :

- Generating piezoelectric effect: Mechanical stress, applied between two surfaces of a solid dielectric part, generates voltage between the surfaces.
- Motor piezoelectric effect: Voltage, applied between two surfaces of a solid dielectric part, results in contracting (expanding) of the part.

Some ceramics (lead zirconate titanate, barium titanate, bismuth titanate, lead magnesium niobate) possess piezoelectric properties.

Piezoelectric ceramics are used for manufacturing various transducers, actuators and sensors like hydrophones, sonar, strain gauges, medical ultrasound equipment.

- **Magnetic properties**

Magnetic Ceramics are prepared by sintering technology from iron oxide and barium/strontium carbonate with small amounts of other metal oxides.

Magnetic Ceramics are called Ferrites.



There are two types of Magnetic Ceramics (Ferrites):

- Isotropic ceramic magnet with equal magnetic properties in all directions
- Anisotropic ceramic magnets with magnetic properties in the direction of pressing.

Ferrites combine good magnetic properties (high magnetization) with very low electrical conductivity. Low conductivity of ferrites allows reducing energy loss, caused by eddy currents, induced in the material when it works in high frequency magnetic fields.

Therefore the widest field of application of ferrites is high frequency appliances: ferritic antennas, speaker magnets, TV deflection-yoke cores and convergence coil cores, Magnetic Resonance Imaging (MRI), audio-visual recording heads.

## 4.- CERAMIC PROCESSING

You can process ceramic through the following methods

- In the form of powder, polycrystalline solids
  - Large numbers of small crystals
  - Parts made with crystals in various orientations
- Single crystal
  - Pure and free from defects
  - You can modify the structure by creation of defects based on the introduction of specific impurities
- Thin film
- Ceramic fibers
  - Fiberglass
  - Silica Fiber

### 4.1 PARTS FORMING FROM CERAMIC POWDER

In the first place you have to make the powder, and then shape it through the different methods. Finally you have sintered in a furnace by heat treatment and make finishing processes.

#### 4.1.1 MANUFACTURE OF CERAMIC POWDER

There are different method:

- Reaction in solid state
- Precipitation from Solutions
- Precipitation from molten
- Precipitation from the vapor phase
- Precipitation from intermediate amorphous
- Special methods
- Reaction in Solid State

This is the method most used, throughout the process will reach high temperatures. The process consists of the following: you have the necessary oxides and carbonates, which are dehydrated at a temperature of 200-800 ° C during 2-5 hours, to be later grinded. After the powders are mixed and compacted, they are already prepared for the heat treatment at high temperatures, 1000-1500 ° C. After one or two grinded, powders have already prepared.

Factors that influence in solid state reactions:

- Thermodynamic conditions
- Structural considerations
- Reaction velocity

Advantages:

- Simple
- Cheap reagents
- Easy stages
- Cheap equipment

Disadvantages:

- Doping during the mixing
- Non-stoichiometry by volatilization of some reactive
- Heterogeneous materials
- Materials with large particle size

#### ● **Precipitation from Solutions**

Advantages:

- Simple
- Increases the homogeneity and the surface area, and particle size decreases
- The particles are in intimate contact in the first stage
- Low temperatures of heat treatment 250-1000 ° C
- Less stable phases at high temperatures

Disadvantages:

- Only suitable for reactive as the water solubility
- Metal ions are precipitated at the same time
- Is not valid if they occur supersaturated solutions
- Materials with large particle size

#### ● **Precipitation from Molten**

This is similar to precipitation from solutions, with the difference that a molten is a liquid at high temperature and a solution is a liquid at room temperature.

It's important to know the phase diagram.

Applications:

- Traditional ceramics (glass)
- Advanced ceramics (crystal growth, abrasive grains based on  $\text{Al}_2\text{O}_3$ )

- **Precipitation from the Vapor Phase**

Advantages:

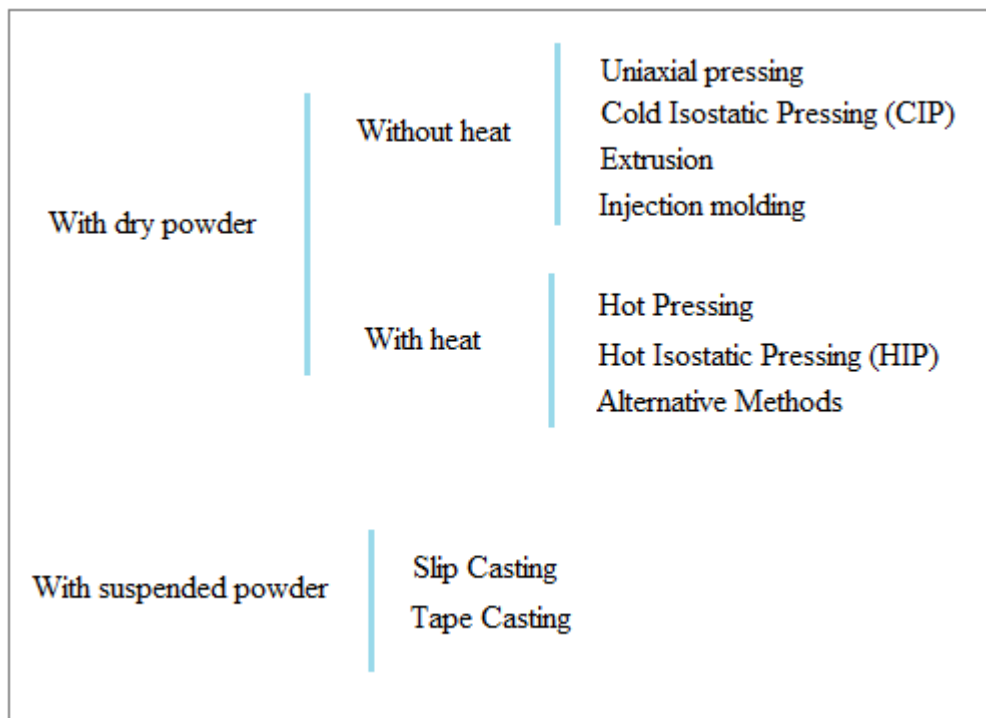
- Large surface area
- Small particle sizes
- High purity
- High reaction velocity
- Spherical phases

Disadvantages:

- Expensive gases
- Very complicated technology
- Expensive process

#### **4.1.2 SHAPE FORMING**

The following techniques are involved in forming ceramic powders into a desired shape:

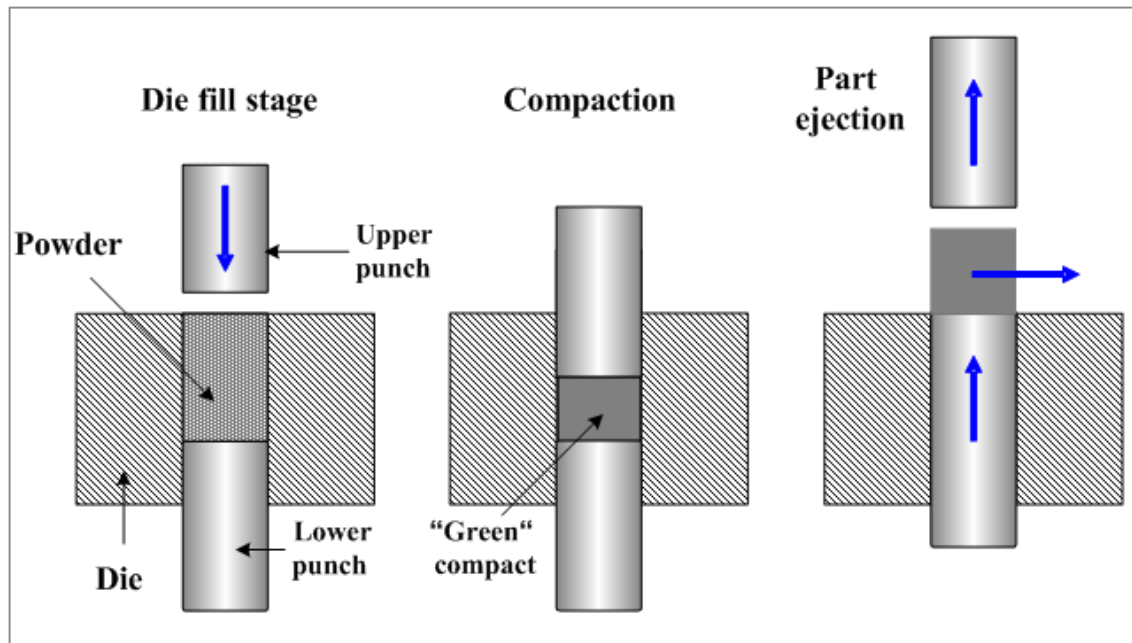


#### 4.1.2.1 UNIAXIAL PRESSING

This shaping method is the powder compaction method involving uniaxial pressure applied to the powder placed in a die between two rigid punches.

Uniaxial pressing is effectively used for mass production of simple parts, and it is inexpensive.

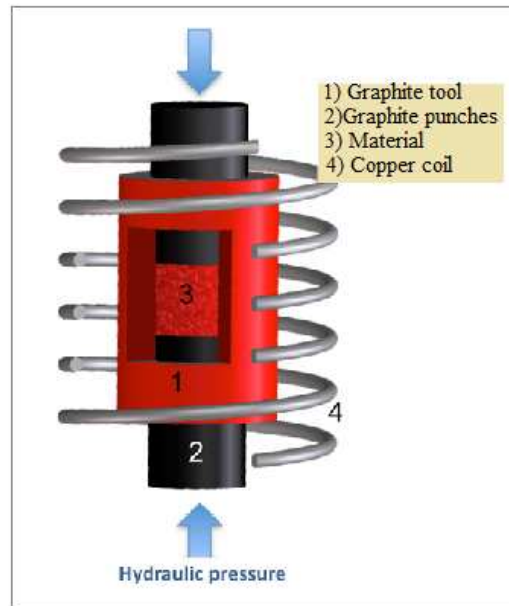
The scheme of the pressing method is:



#### 4.1.2.2 HOT PRESSING

This forming technique is the simultaneous application of external pressure and temperature to enhance densification. It is conducted by placing either powder or a compacted preform into a suitable die, typically graphite, and applying uniaxial pressure while the entire system is held at an elevated temperature, e.g. 2000°C for SiC. Hot pressing is mainly used to fabricate hard and brittle materials.

Within hot pressing technology, three distinctly different types of heating can be found in use: induction heating, indirect resistance heating, and direct hot pressing.

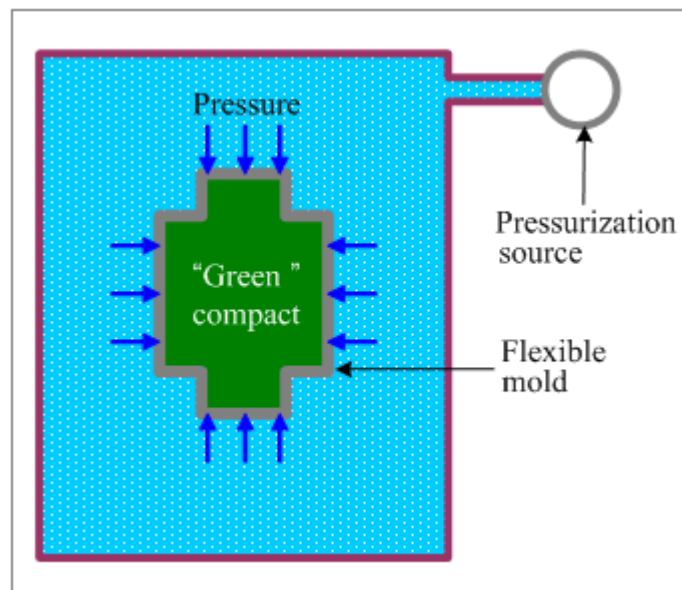


#### 4.1.2.3 COLD ISOSTATIC PRESSING (CIP)

Cold isostatic pressing (CIP) is conducted at room temperature.

A flexible mold immersed in a pressurized liquid medium is used in the cold isostatic pressing method

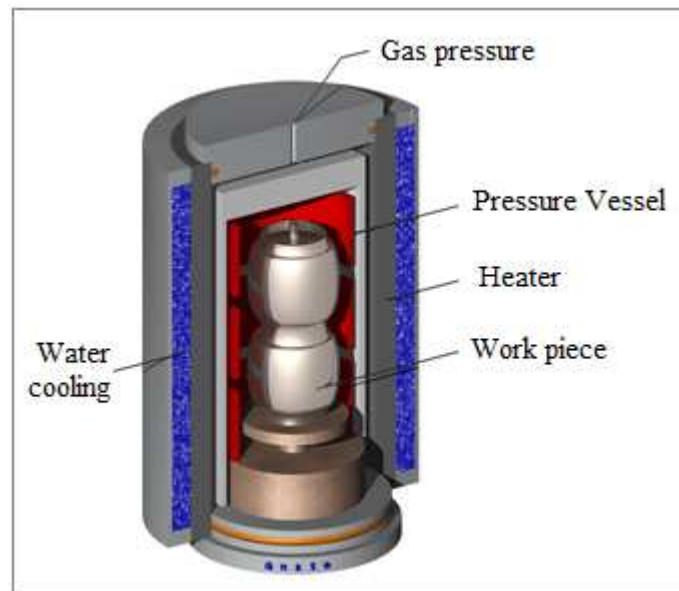
The cold isostatic pressing (CIP) method has the following advantages as compared to the die cold pressing method: better uniformity of compaction and more complex forms may be compacted.



#### 4.1.2.4 HOT ISOSTATIC PRESSING (HIP)

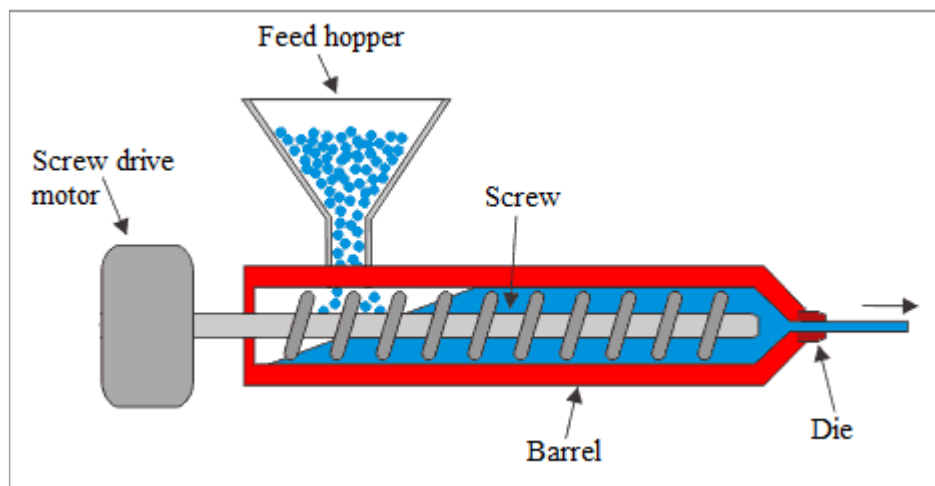
Hot isostatic pressing (HIP) involves isostatic pressing conducted at increased temperature. As a pressure medium a gas is used.

Hot isostatic method (HIP) combines pressing and sintering, causing consolidation of powder particles, healing voids and pores. The part shrinks and densifies, forming sound high strength structure.



#### 4.1.2.5 EXTRUSION

This forming process consists of forcing a plastic mix of a ceramic powder through a constricting die to produce elongated shapes that have a constant cross-section. The powder mix consists of a fine ceramic powder with the appropriate additions of binders and plasticisers to give the desired flow properties (rheology), either cold or when heated prior to being forced through the die.

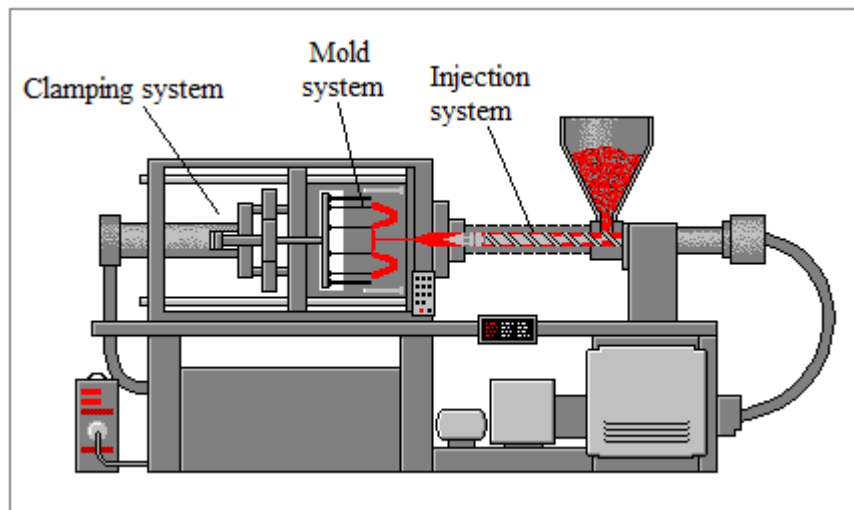


#### 4.1.2.6 INJECTION MOLDING

Injection molding is the method of compaction of ceramic powder fed and injected into a mold cavity by means of a screw rotating in cylinder. The method is similar to the plastic injection molding. This method is widely used for manufacturing small parts having complex shapes.

The processing technology comprises the following stages:

- Mixing the ceramic powder with 30% - 40% of a binder – low melt polymer.
- Injection of the warm powder with molten binder into the mold by means of the screw.
- Removal of the part from the mold after cooling down of the mixture.
- Debinding – removal of the binder. There are two debinding methods:
  - Solvent debinding – the binder is dissolved by a solvent or by water;
  - Thermal debinding – the binder is heated above the volatilization temperature.
- Sintering the “green” compact.

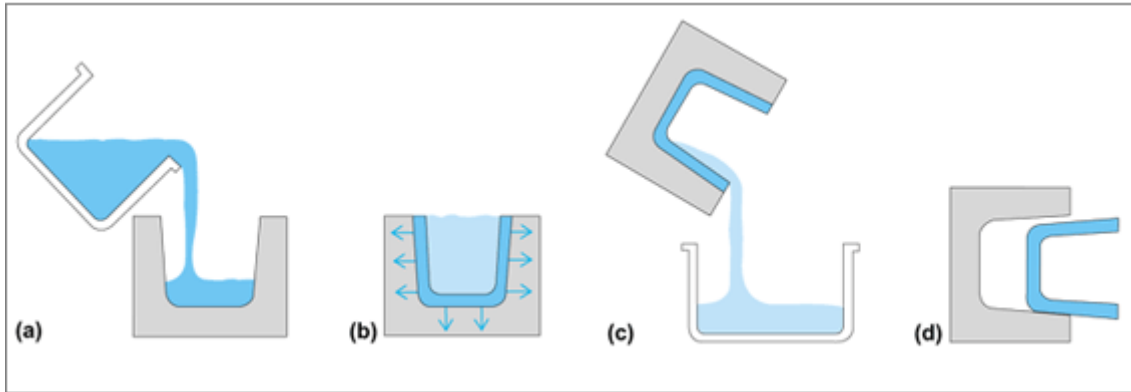


#### 4.1.2.7 SLIP CASTING

Slip casting refers to the filling of a mould, a negative of the desired shape, with a slip consisting of a suspension of micrometer size ceramic particles in liquid.

The capillary action due to the pores in the mould withdraws the liquid from the slip. As the liquid filters into the mould a cast is formed on the mould surface. Stable slips with high solids contents and low viscosity's can be prepared by careful adjustments of the chemistry of the slip by adding deflocculants.

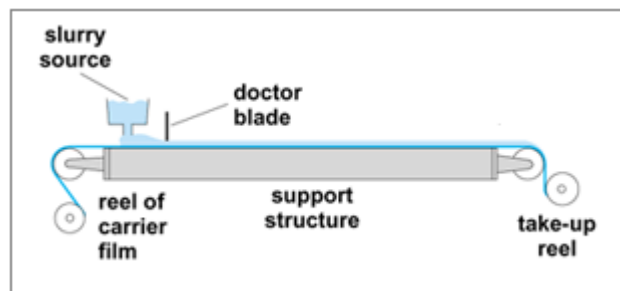




#### 4.1.2.8 TAPE CASTING

This process involves the casting of a slurry onto a flat moving carrier surface. The slurry usually consists of a ceramic powder with the appropriate additions of solvents plasticisers and binders.

The slurry passes beneath the knife edge as the carrier surface advances along a supporting table. The solvents evaporate to leave a relatively dense flexible sheet that may be stored on rolls or stripped from the carrier in a continuous process.



#### 4.1.3 SINTERING

Sintering of ceramic materials is the method involving consolidation of ceramic powder particles by heating the green compact part to a high temperature below the melting point, when the material of the separate particles diffuse to the neighbouring powder particles.

The driving force of sintering process is reduction of surface energy of the particles caused by decreasing their vapour-solid interfaces.

During the diffusion process the pores, taking place in the green compact, diminish or even close up, resulting in densification of the part, improvement of its mechanical properties.

Decrease of the porosity, caused by the sintering process, is determined by the level of the initial porosity of the green compact, sintering temperature and time. Sintering is enhanced if a liquid phase takes part in the process (liquid phase sintering).

Sintering of pure oxide ceramics require relatively long time and high temperature because the diffusion proceeds in solid state. Applying pressure decreases sintering time and the resulted porosity.

## 4.2 THIN FILM

A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. Electronic semiconductor devices and optical coatings are the main applications benefiting from thin film construction.

Work is being done with ferromagnetic and ferroelectric thin films for use as computer memory.

Ceramic thin films are in wide use. The relatively high hardness and inertness of ceramic materials make this type of thin coating of interest for protection of substrate materials against corrosion, oxidation and wear. In particular, the use of such coatings on cutting tools can extend the life of these items by several orders of magnitude.

Advantages:

- Use less material, so costs are reduced
- Properties in many cases superior to the materials in a volumetric form
- Allows design and implement microstructures with properties unavailable in volumetric materials
- You get interesting combinations of properties with an appropriate substrate and the film grown

Methods of obtaining:

- Chemical and electrochemical methods:
  - Sputter deposition
  - Anodic oxidation
  - CVD (Chemical Vapour Deposition)
  - Thermal oxidation
- Physical methods
  - Sputtering
  - Vacuum deposition

#### 4.2.1 CHEMICAL AND ELECTROCHEMICAL METHODS

There is a reaction of gas or vapor over the surface of the substrate, followed by a nucleation and growth stage.

- **Sputter deposition**

Metal films are obtained. Two electrodes are immersed in a bath with an electrolyte solution. When applying a voltage between the electrodes, the metal ions of the solution were deposited on the cathode. In order to maintain electroneutrality, the metal anode gradually dissolves.

- **Anodic oxidation**

Oxidized films over metallic substrates: Al, Ta, Nb, Ti and Zr

Metal anode immersed in electrolyte solvents or acid solutions. Oxygen ions are attracted to the anode forming a thin layer (eg  $\text{Al}_2\text{O}_3$ ). Increasing the difference of potential, it is favored the phenomenon of diffusion and increased the thickness of the film layer.

- **Thermal oxidation**

Films of compounds resulting from oxidation at high temperature and in air.

- **Chemical Vapour Deposition (CVD)**

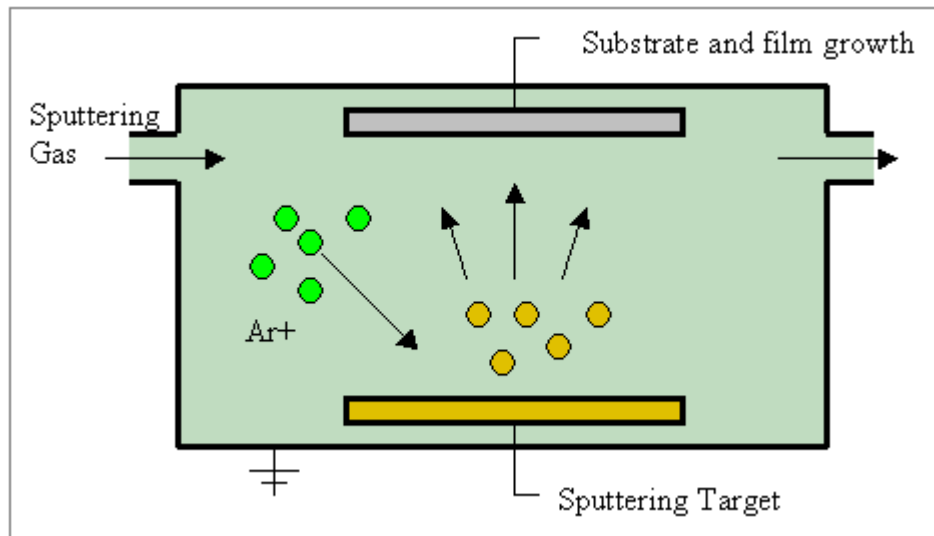
Chemical vapor deposition (CVD) is a chemical process used to produce high-purity, high-performance solid materials. The process is often used in the semiconductor industry to produce thin films. In a typical CVD process, the wafer is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit.

#### 4.2.2 PHYSICAL METHODS

The film is formed on the substrate in a process of nucleation and growth, through a phenomenon of chemical adhesion

- **Sputtering**

Surface atoms of the target (cathode) are started by a bombardment of high energy ions. These atoms are deposited on the substrate or the neighborhood (conductor) forming a thin film.



- **Vacuum deposition**

Vacuum deposition is used to deposit layers atom-by-atom or molecule-by-molecule at sub-atmospheric pressure (vacuum) on a solid surface. The layers may be as thin as one atom to millimetres thick (freestanding structures). There may be multiple layers of different materials (e.g. optical coatings).

### 4.3 SINGLE CRYSTAL

A single crystal or monocrystalline solid is a material in which the crystal lattice of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries. The absence of the defects associated with grain boundaries can give monocrystals unique properties, particularly mechanical, optical and electrical, which can also be anisotropic, depending on the type of crystallographic structure. These properties, in addition to making them precious in some gems, are industrially used in technological applications, especially in optics and electronics.

- **Manufacture, Czochralski process**

The Czochralski process is a method of crystal growth used to obtain single crystals of semiconductors (e.g. silicon, germanium and gallium arsenide), metals (e.g. palladium, platinum, silver, gold), salts, and synthetic gemstones.

The most important application may be the growth of large cylindrical ingots, or boules, of single crystal silicon. Other semiconductors, such as gallium arsenide, can also be grown by this method.

The method involves growing a single crystal from a melt of the same composition. A seed is placed in contact with the surface of the melt at a temperature slightly above the melting temperature. The seed is stretched out from the melt, causing the solidification on the surface of the seed in the same crystallographic orientation as the seed. The melt and the seed are rotated in opposite directions while maintaining constant temperature.

#### 4.4 CERAMIC FIBERS

There are many kinds of fibers, in the next table you can see some fibers and his properties:

Material	Density (g/cm <sup>3</sup> )	Tensile Strength (Gpa)	Young's Modulus (x10 <sup>6</sup> GPa)	Fusion temperature (°C)
Glass E	2,55	3,4	72	<1725
Glass S	2,5	4,5	87	<1725
Carbon HS	1,75	5,6	276	3700
Carbon HM	1,9	1,9	531	3700
Al <sub>2</sub> O <sub>3</sub>	3,95	2,1	379	2015
B <sub>4</sub> C	2,36	2,3	483	2450
SiC	3	3,9	483	2700
ZrO <sub>2</sub>	4,84	2,1	345	2677

##### 4.4.1 GLASS FIBER

- Composition

SiO<sub>2</sub> (50-70%) + oxides Ca, Al, B, Na, Mg y K

- Properties

- Noncombustible
- Good Chemicals resistance
- Good biological resistance
- Good thermal resistance
- Thermal insulation
- Electrical insulation
- Low coefficient of expansion
- Low cost

- Manufacturing processes

There are two main types of glass fiber manufacture and two main types of glass fiber product. First, fiber is made either from a direct melt process or a marble remelt process. Both start with the raw materials in solid form. The materials are mixed together and melted in a furnace. Then, for the marble process, the molten material is sheared and rolled into marbles which are cooled and packaged. The marbles are taken to the fiber manufacturing facility where they are inserted into a can and remelted.

The molten glass is extruded to the bushing to be formed into fiber. In the direct melt process, the molten glass in the furnace goes right to the bushing for formation.



#### 4.4.2 CARBON FIBER

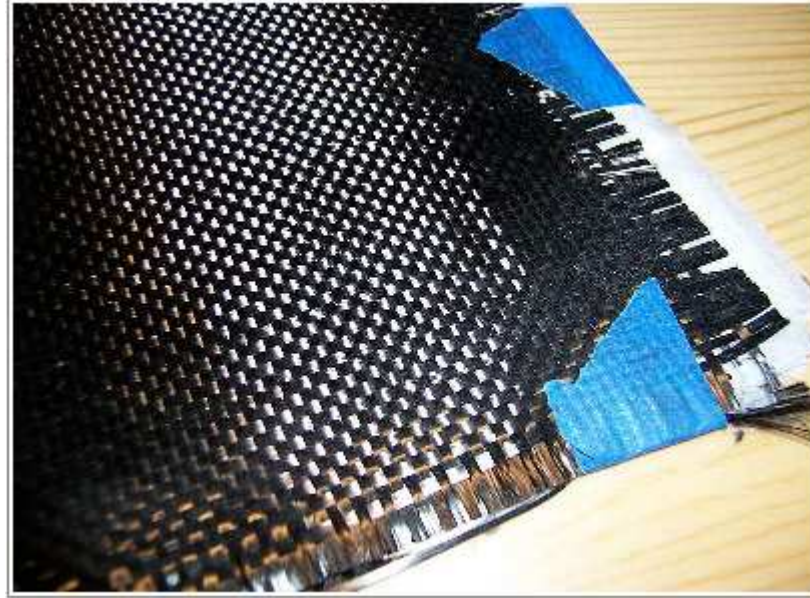
Carbon fiber is a thin, fibrous material with a micro graphite crystal structure composed of carbon atoms. The atoms are aligned parallel to the long axis of the fiber, making it extremely strong for its size. Carbon fibers have very good mechanical and physical properties, like high thermal conductivity.

Carbon fibers are classified into three classes:

- PAN-based, for those made of polyacrylonitrile resin,
- Pitch-based, for those made of oil or coal pitch and
- Rayon-based, for those made of textile material.

They also have different properties depending upon the precursor used to make the fiber. Carbon fibers are rarely used individually, but as reinforcement and/or functionality of composite materials made with resin, ceramic or other materials.

They are used in such diverse areas as structural components (aircrafts, automobiles), sporting goods (golf shafts, bicycle frames), or as construction material (reinforced concrete). In carbon fibers is very important its low price, making them much more accessible.



#### **4.4.3 CERAMIC FIBER**

These fibers appear from the need for reinforcements in aerospace industry for high temperatures ( $T > 1300^{\circ}\text{C}$ ) and thermal shock. Besides this resistance, these fibers present very high performances regarding tensile strength and chemical stability. However, their manufacture and manipulation is extremely complicated and expensive (5 times more expensive than carbon fibers), so its use has been limited to this industry and the metal industry, in carburizing furnace for thermochemical treatments.

## 5.- ADVANCED CERAMICS

### 5.1 STRUCTURAL CERAMICS

#### 5.1.1 OXIDE CERAMICS

##### 5.1.1.1 ALUMINA

Aluminium Oxide ( $\text{Al}_2\text{O}_3$ ) or alumina is one of the most versatile of refractory ceramic oxides and finds use in a wide range of applications.

It is found in nature as corundum in emery, topaz, amethyst, and emerald and as the precious gemstones ruby and sapphire, but it is from the more abundant ores such as bauxite, cryolite and clays that the material is commercially extracted and purified.

Small amounts of silica ( $\text{SiO}_2$ ), magnesia ( $\text{MgO}$ ) and zirconia ( $\text{ZrO}_2$ ) may be added to alumina ceramics. Addition of zirconia to alumina ceramic results in considerable increase of the material fracture toughness.

- **Properties**

Alumina possesses strong ionic bonding, which determines the material properties:

- High mechanical strength (flexural strength) and hardness
- High wear resistance
- High resistance to chemical attacks of strong acids and alkali even at high temperatures
- High stiffness
- Excellent insulating properties
- Low coefficient of thermal expansion
- Good fracture toughness
- Good thermal conductivity
- Good biocompatibility

The properties are function of degree of purity and porosity.

- **Structure**

The most common form of crystalline alumina is known as corundum. The oxygen ions nearly form a hexagonal close-packed structure with aluminium ions filling two thirds of the octahedral interstices.

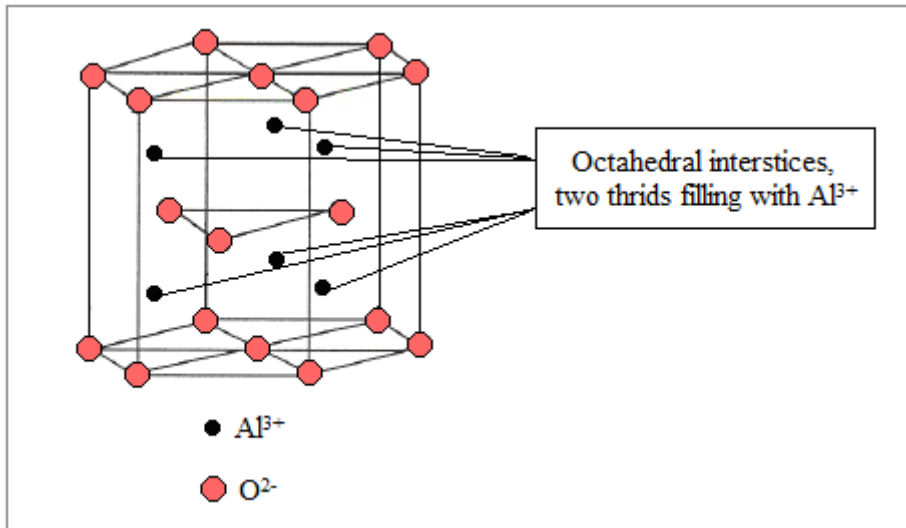
Alumina also exists in other phases, these other phases appear in function of mineral of departure and the process of obtaining the alumina.

Boehmite  $\rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$

Gibbsite  $\rightarrow \gamma \rightarrow \tau \rightarrow \kappa \rightarrow \theta \rightarrow \alpha$

Diaspore  $\rightarrow \alpha\text{-Al}_2\text{O}_3$

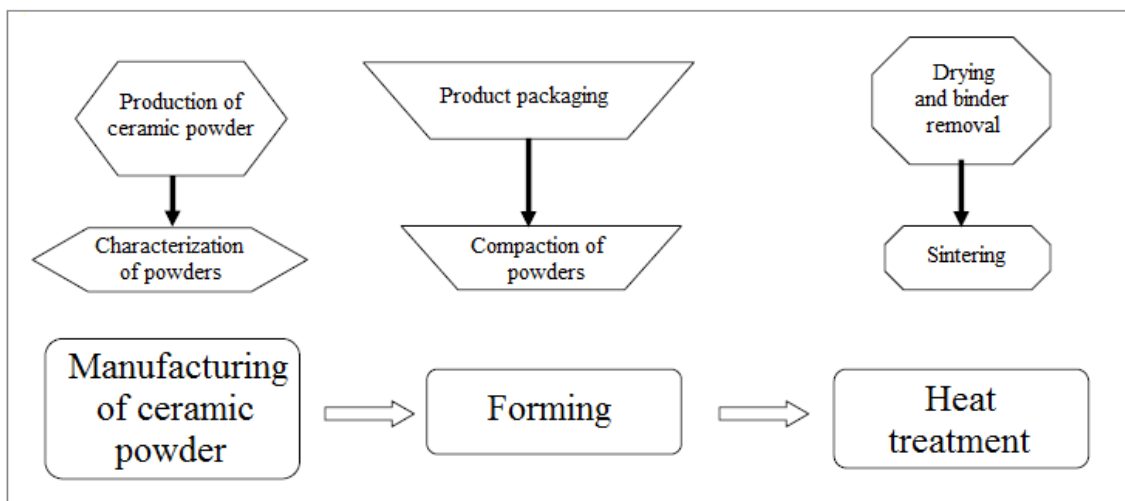




### • Applications

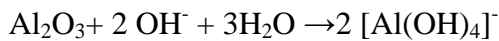
% $\text{Al}_2\text{O}_3$	Grain size	Porosity	Applications Area
>99.6	Fine	closed	Electrical, Engineering, Biomedical
>99.8	Fine	zero	Lamp tubes, Optical
>99.6* (recrystallised)	Medium	closed	High temperature uses
95 – 99.5	Fine	closed	General electrical, engineering
80 - 95	Fine	closed	Low duty electrical (spark plugs)
90 - 99.6	Fine/Coarse	open	Filter media
80 - 90	Fine/Coarse	open	Abrasive

### • Production

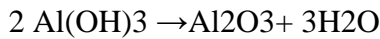


Production of alumina powder:

Bauxite (boehmite, gibbsite, diaspor) is purified by the Bayer process:



The solid is then calcined (heated strongly) to give aluminium oxide:



Aluminum ceramics parts are manufactured by the following technologies: uniaxial pressing, isostatic pressing, injection molding, extrusion, slip casting and tape casting. The parts may be machined in "green" condition before sintering.

- **Sintering**

There are two types of sintering:

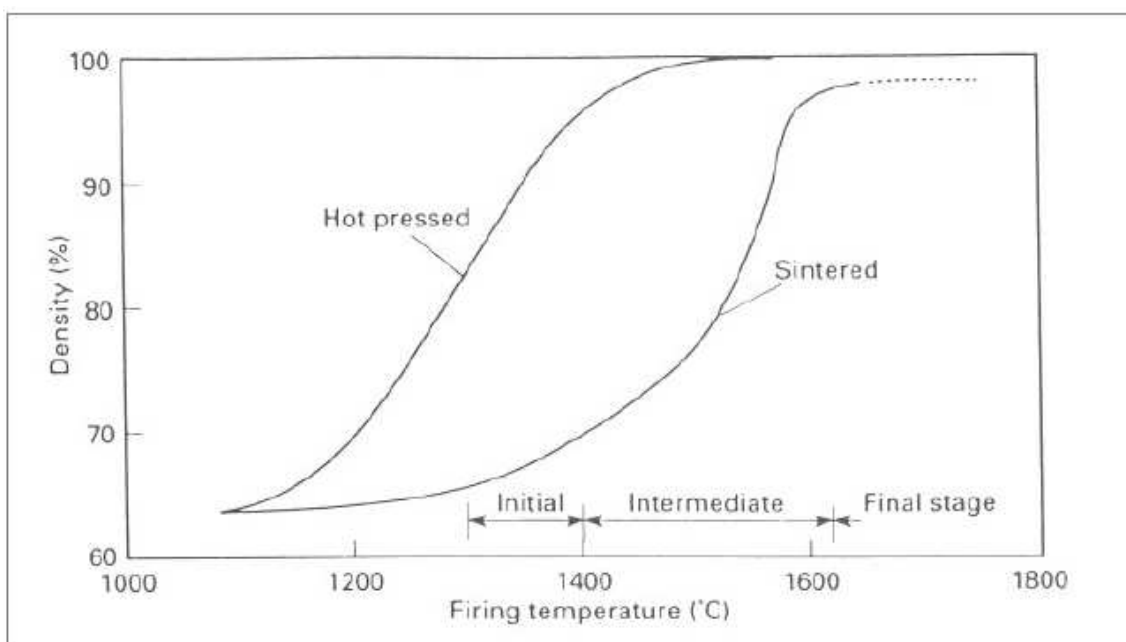
- Solid state sintering (SSS): >99,7%  $\text{Al}_2\text{O}_3$
- Liquid phase sintering (LPS): 80-99,7%  $\text{Al}_2\text{O}_3$

**a) Solid state sintering (SSS):**

Effects of sintering on the piece:

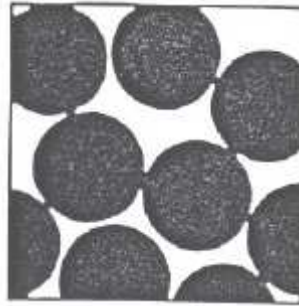
- Elimination of pores
- Reduction of the piece
- Increase the density

There are three stages:

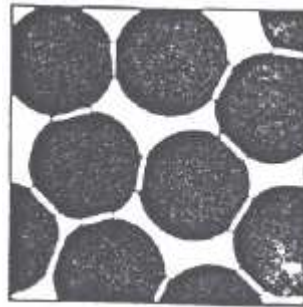


Effects of sintering at the micro-structural level are changes in grain size and shape, and changes in pore size and shape.

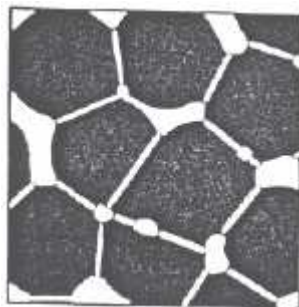
- Loose powder particles



- Initial stage: the following events occurs, training collars, rearrangement of particles and little change in density



- Intermediate stage: collars grow and reduces the porosity



- Final stage: there is a grain growth and porosity drops slightly



**b) Liquid phase sintering (LPS)**

It is characterized by having variable contents of forming additives the liquid phase:

- Silicates of Ca and/or Mg
- Aluminosilicates of Ba
- $\text{MnO}_2/\text{TiO}_2$

Classification:

- **99-99.7%**, its applications are hip prosthesis and electrical insulation



- **94.5-99.7%**

In this range highlights the presence of aluminosilicates more CaO and/or MgO by increasing the percentage of liquid vitreous.

Secondary phases also appear as a function of temperature, composition and cooling rate

- Anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ )
- Gehlenite ( $\text{CaAl}_2\text{SiO}_6$ )
- Hexaaluminate Ca ( $\text{CaAl}_{12}\text{O}_9$ )
- Spinel ( $\text{MgAl}_2\text{O}_4$ )
- Mullite ( $2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3$ )
- Cordierite ( $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ )

Its applications are electrical insulation and computer circuit substrates.

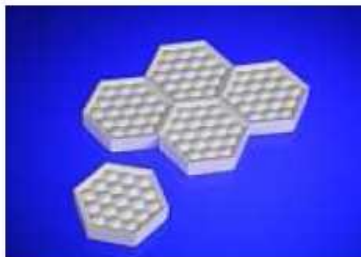
- **80-94.5%**

T sintering < 1500 °C

Its applications are electrical insulation, refractory and low-temperature mechanical components.

- **Examples of applications**

- Insulators for spark plugs
- Wear resistant pieces
- Electrical and electronic industry components
- Abrasives materials
- Refractory materials
- Bioceramics
- Catalysis and absorbent
- Ceramic matrix composites
- Plates for shielding



Light vehicle protection



Ballistic vest



Alumina and aramid for ballistic vest

- High temperature resistant parts



Crucibles



Thermocouple protection



- Cutting tools



### 5.1.1.2 ZIRCONIA

Zirconia ( $\text{ZrO}_2$ ) is a white crystalline oxide of zirconium. Its most naturally occurring form, with a monoclinic crystalline structure, is the rare mineral baddeleyite.

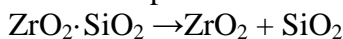
- **Properties**

- High density – up to  $6.1 \cdot 10^3 \text{ kg/m}^3$
- Low thermal conductivity – 10% of that of alumina ceramics
- High fracture toughness
- Very high flexural strength and hardness
- High maximum service temperature – up to  $2400^\circ\text{C}$
- Coefficient of thermal expansion similar to that of cast iron
- Modulus of elasticity similar to steel;
- High chemical resistance;
- High resistance
- Good wear resistance
- Low coefficient of friction
- Oxygen ion conductivity (used for oxygen sensors and high temperature fuel cells)
- Electrical insulation

- **Obtaining ceramic powder**

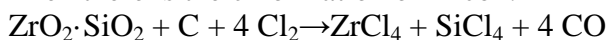
To obtain zirconia powder are needed minerals zircon ( $\text{ZrO}_2 \cdot \text{SiO}_2$ ) and baddeleyite ( $\text{ZrO}_2$  impure monoclinic)

In the first place occurs the thermal decomposition of zircon:



Where  $\text{SiO}_2$  is dissolved in boiling  $\text{Na}(\text{OH})$

Then there is the chlorination of zircon:



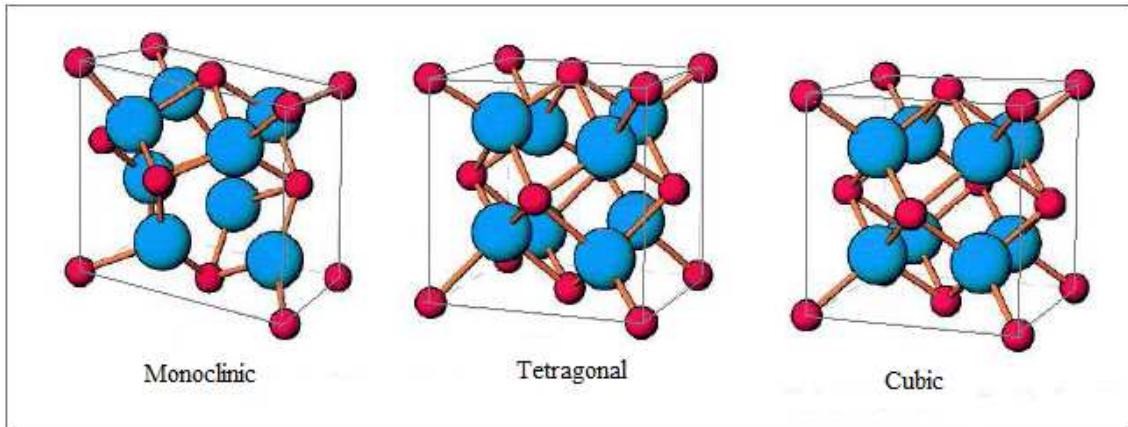
Where:  $\text{SiCl}_4 + 4 \text{CO}$  are volatile matters

$\text{ZrCl}_4$ , by hydrolysis obtain  $\text{ZrO}_2$

- **Structure and polymorphism**

Pure zirconia changes its crystal structure depending on the temperature, and has three well-defined crystalline polymorphs: monocyclic phases, tetragonal, and cubic.

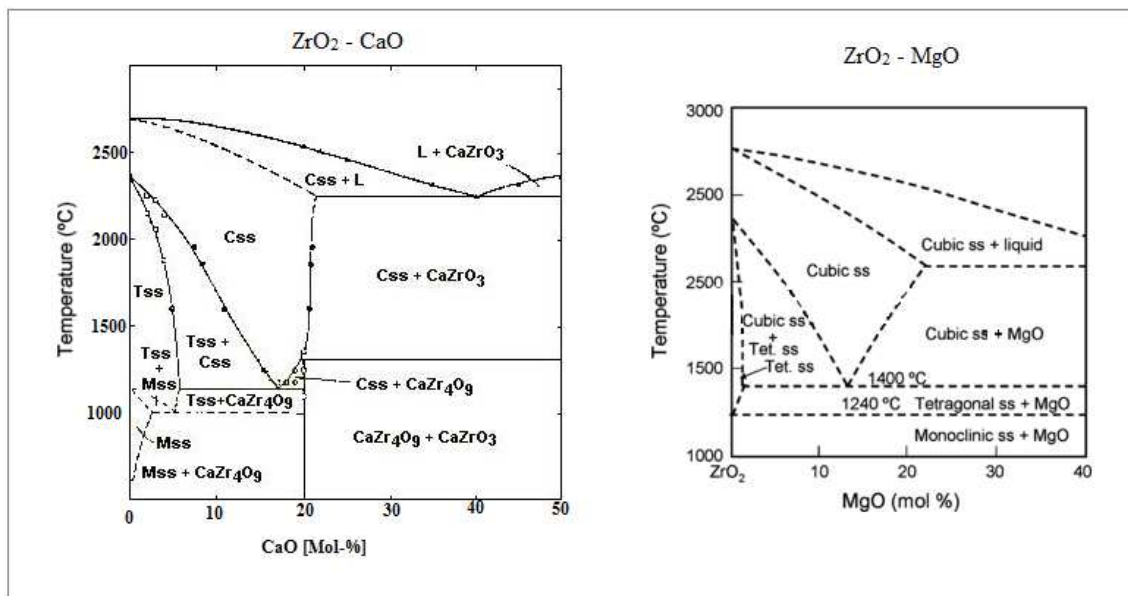
Monoclinic phase is stable up to  $1170^\circ\text{C}$  where it is transformed to the tetragonal phase. At  $2370^\circ\text{C}$  the tetragonal form transforms to the cubic phase, which exists until  $2680^\circ\text{C}$ , the melting point of zirconia.



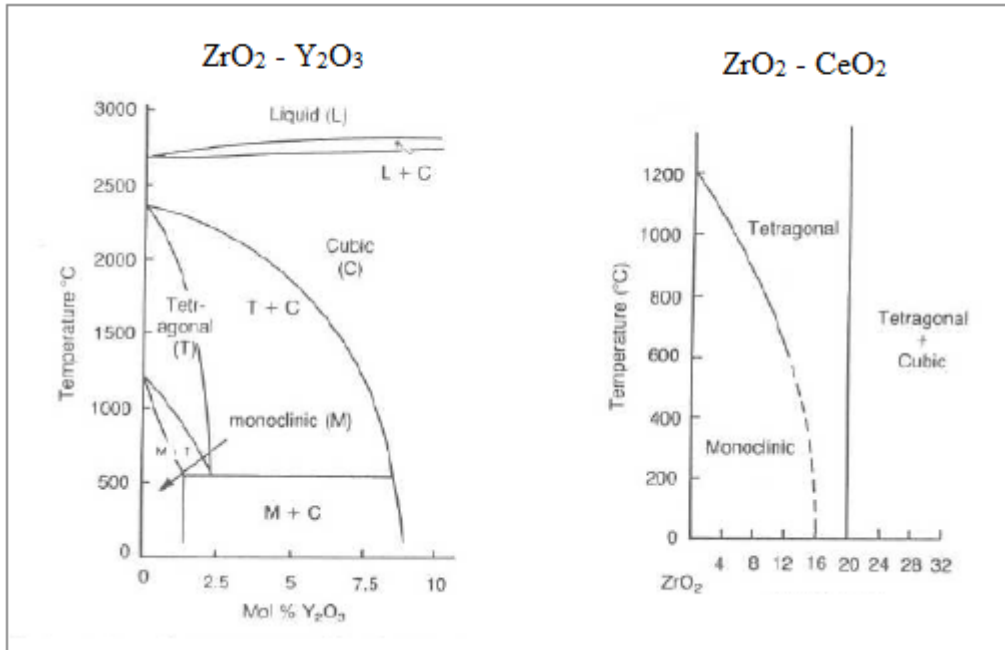
It is also important to know that zirconia suffers a significant change in volume when going from a crystalline structure to another, changed are about 4.6%.

The volume change of the transformation can be used to advantage by adding stabilisers cubic oxides. The most common are CaO, MgO, CeO<sub>2</sub>, and Y<sub>2</sub>O<sub>3</sub>

Below are shown the phase diagrams of ZrO<sub>2</sub> - Stabiliser







- **Types of Zirconia**

Material	Abbrev.
Tetragonal Zirconia Polycrystals	TZP
Partially Stabilised Zirconia	PSZ
Fully Stabilised Zirconia	FSZ
Transformation Toughened Ceramics	TTC
Zirconia Toughened Alumina	ZTA
Transformation Toughened Zirconia	TTZ

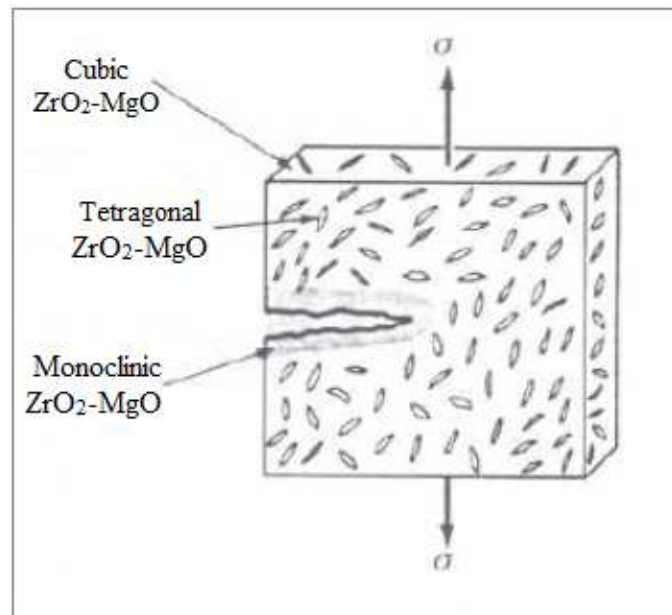
The most important are PSZ, FSZ and TZP.

**Partially stabilized zirconia (PSZ)**

In the cooling of the transformation of tetragonal to monocyclic, there is a large volume increase (3-5%). This change is enough to cause cracks. So, the manufacture of large components of pure zirconia is not possible. We can be used it to advantage by adding stabilisers cubic oxides. These oxides can stabilize the cubic form below room temperature. Therefore, if you add an insufficient amount of stabilising oxide, the material is processed correctly, the zirconia particles can be stored in metastable tetragonal form at room temperature. These materials are PSZ.

During the use of stress, for example in the region of a crack to propagate, metastable tetragonal particles transform into stable monocyclic stage. The extent of the volume is placed in the region around the particles adjacent to the crack, compression, and slow crack propagation until the applied voltage is increased.





### **Fully stabilized zirconia (FSZ)**

It has cubic crystal structure.

### **Polycrystalline tetragonal zirconia (TZP)**

A third type of ceramic material is formed using a low concentration of yttria (Y<sub>2</sub>O<sub>3</sub>). TZP is metastable tetragonal structure of very fine zirconia grains sintered at low temperature.

- **Applications**

- **Knives and scissors**

A major problem with metal knives and scissors when faced with tough materials such as Kevlar or when cutting large quantities of paper (which often contain dispersed minerals) is the abrasion or blunting of the cutting edge. Zirconia materials in this application retain their edge and stay sharp longer.

Other similar applications include blades for cutting of plastic film, magnetic tape and other tough or abrasive materials. Zirconia is also used in composite cutting tools and abrasive wheels.



- **Seals, valves and pump impellers**

The handling and transport of slurries and aggressive chemicals present a difficult materials problem. High temperatures and high pressure flow lead to highly reactive and abrasive conditions.

- **Orthopaedic implants**

Zirconia is used as a femoral head component in hip implants. High strength and high toughness allow the hip joint to be made smaller which allows a greater degree of articulation. The ability to be polished to a high surface finish also allows a low friction joint to be manufactured for articulating joints such as the hip. The chemical inertness of the material to the physiological environment reduces the risk of infection.

- **Refractory applications**

Zirconia (monoclinic and partially stabilised) powder is used in refractory compositions to enhance thermal shock resistance and abrasion resistance. These materials are used in severe applications such as sliding gate plates for pouring steel, and in steel immersion applications such as stopper rods and as components in submerged entry nozzles. Other refractory applications for zirconia include insulating fibre and thermal barrier coatings.

- **Electronic and electrical applications**

The electronic and electrical applications of zirconia rely on the relatively high electronic conductivity and the high oxygen ion conductivity of the fully stabilised material.

This allows the material to be used as resistive heating elements (which can be operated in air beyond the temperature range of convention elements), oxygen sensors which operate on the Nernst cell principle, and electrolyte in solid oxide fuel cells.

- **Synthetic Gemstones**

By melting zirconia with dopants and recrystallising on cooling, gemstones can be produced which simulate diamond, ruby, topaz and emerald. These materials are commonly known as cubic zirconias.

- **Other Applications**

Due to its excellent wear resistance, zirconia is used as in thread guide, cams and wire drawing dies. It is also used as a cathode for plasma torches and a nucleating agent for glass ceramics.

## 5.1.2 NON-OXIDE CERAMICS

### 5.1.2.1 CARBIDES

The main properties of carbides are:

- High hardness
- Inert
- High melting temperature
- High temperature decomposition
- High thermal conductivity
- Low coefficient of thermal expansion

And its principal applications are:

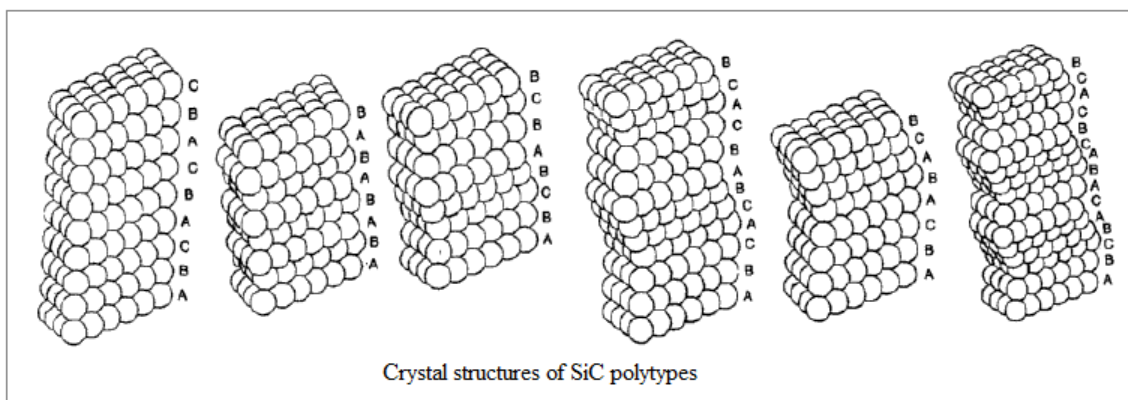
- Abrasives (main application)
- Components of different wear resistant machinery
- Bearings
- Gas turbine components operating at high temperature adjusting valves
- Resistance Furnace
- Semiconductor
- Protection and armament industry

Some of the most typical carbides are SiC, WC, TiC and TaC.

#### ➤ Silicon Carbide (SiC)

##### ● Structure of SiC

Many structures or polytypes (specifically 70) have been identified for Silicon Carbide. These polytypes have different stacking arrangements for the atoms of silicon and carbon in the compound. One of the simplest structures is the diamond structure, which is known as  $\beta$ -SiC. There are more complex hexagonal or rhombic structures of the compound and these are designated as  $\alpha$ -SiC.



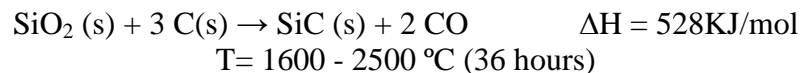
- **Properties of SiC**

By far the most important carbide ceramics are materials based on silicon carbide (SiC). Diverse types are manufactured, depending on the intended purpose, but all are characterised by the typical properties of silicon carbide, such as:

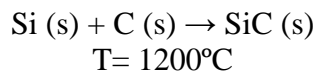
- Very high hardness
- Corrosion resistance, even at high temperatures
- High resistance to wear
- High strength, even at high temperatures
- Resistance to oxidation even at very high temperatures
- Good thermal shock resistance
- Low thermal expansion
- Very high thermal conductivity
- Good tribological properties and
- Semiconducting properties

- **Synthesis of SiC powder**

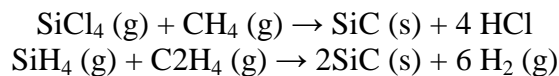
- Acheson process: The process consists of heating a mixture of clay and powdered coke (carbon) in an iron bowl.



- Direct reaction



- Vapor phase reactions



- **Production of SiC**

Depending on the manufacturing technique, it is necessary to distinguish between self-bonded and second-phase bonded silicon carbide ceramics, as well as between open porous and dense types:

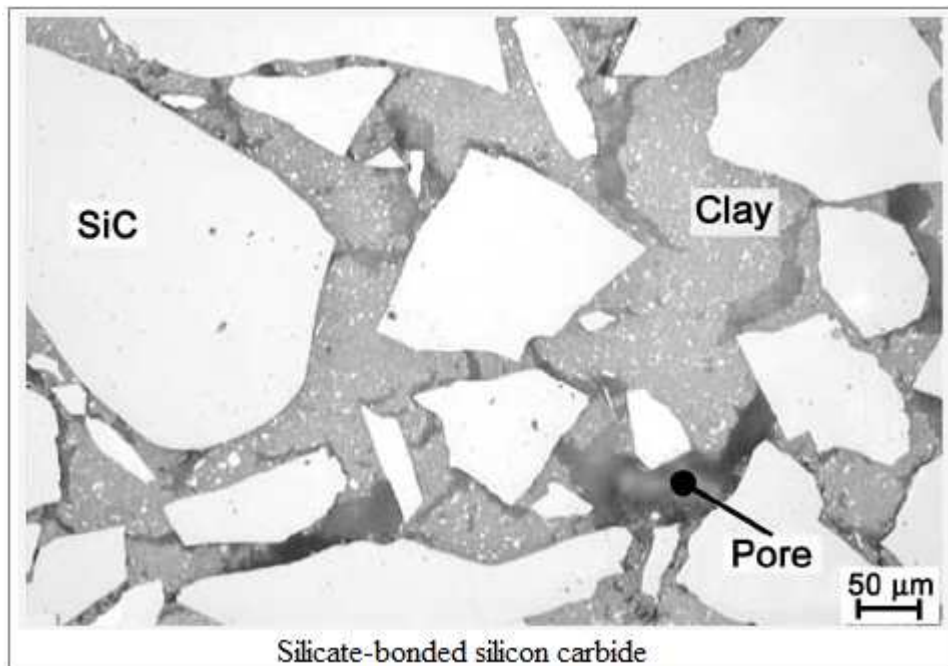
**Open porous silicon carbide**

- Silicate-bonded silicon carbide
- Recrystallized silicon carbide (RSiC)
- Nitride bonded silicon carbide (NSiC)

### Dense silicon carbide

- Reaction-bonded silicon carbide (RBSiC)
  - Silicon-infiltrated silicon carbide (SiSiC)
  - Sintered silicon carbide (SSiC)
  - Hot pressed silicon carbide (HPSiC)
  - Liquid-phase sintered silicon carbide (LPSiC)
- 
- **Silicate-bonded silicon carbide**

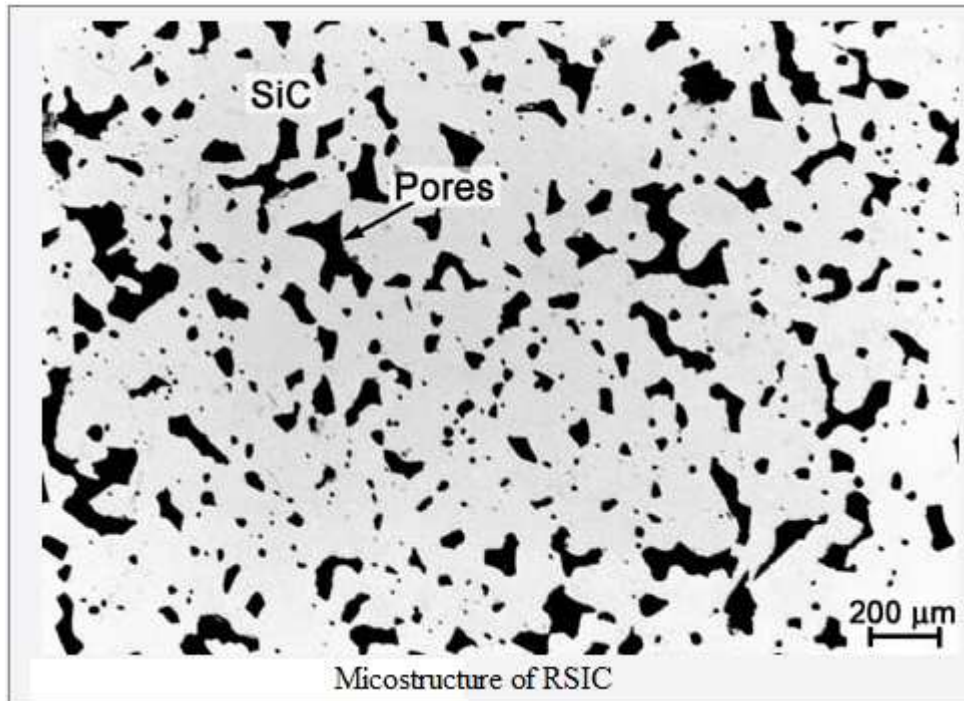
Silicate bonded silicon carbide is manufactured from coarse and medium grained SiC powders, sintered with 5 to 15 % aluminosilicate binder in air. However, strength, corrosion resistance, and above all the high-temperature characteristics, are determined by the silicate binding matrix, and lie below those of non-oxide bonded SiC ceramics. The advantage lies in the comparatively low manufacturing cost. Applications for this material include, for example, plate stackers used in the manufacture of porcelain.



- **Recrystallized silicon carbide (RSiC)**

Recrystallized silicon carbide (RSiC) is a pure silicon carbide material with approximately 11 to 15 % open porosity. This material is sintered at very high temperatures from 2300 to 2500° C. As a result of its open porosity, RSIC possesses lower strength in comparison to dense silicon carbide ceramics and it does not resist oxidation over long periods, and is subject to a certain amount of corrosion when applied as kiln furniture or as a heating element. The maximum application temperature lies between 1600 and 1650° C.

Due to its porosity, RSiC demonstrates outstanding thermal shock resistance. It allows the manufacture of large parts that are used primarily as heavy kiln furniture (beams, rollers, supports etc.), for example in the porcelain industry.



- **Nitride bonded silicon carbide (NSiC)**

It is a porous material, having a porosity of between 10 and 15 %, of which between 1 and 5 % is opened porosity. The manufacturing process involves a moulded body of silicon carbide granulate and metallic silicon powder being nitrided in an atmosphere of nitrogen at approx. 1400 °C. The material is then exposed to an oxidising atmosphere at a temperature above 1200 °C. In this way a thin oxidation layer of glass is created.

The bending strength of NSiC is greater, because the pore size is smaller than that of RSiC. It is also more resistant to oxidation, while the tougher surface means that it does not deform during its service life. This material is particularly suitable for use in highly stressed kiln furniture at up to 1500°C.

- **Silicon-infiltrated silicon carbide (SiSiC)**

It is composed of approximately 85 to 94 % SiC and correspondingly 15 to 6 % metallic silicon (Si). SiSiC has practically no residual porosity.

This is achieved by infiltrating a formed part of silicon carbide and carbon with metallic silicon. The advantage of this technique is that, unusually large parts with very precise dimensions can be manufactured. The application of SiSiC is limited to approximately 1380° C due to the melting point of metallic silicon. Below this temperature, SiSiC exhibits very high strength and corrosion resistance combined with good thermal shock resistance and wear resistance.

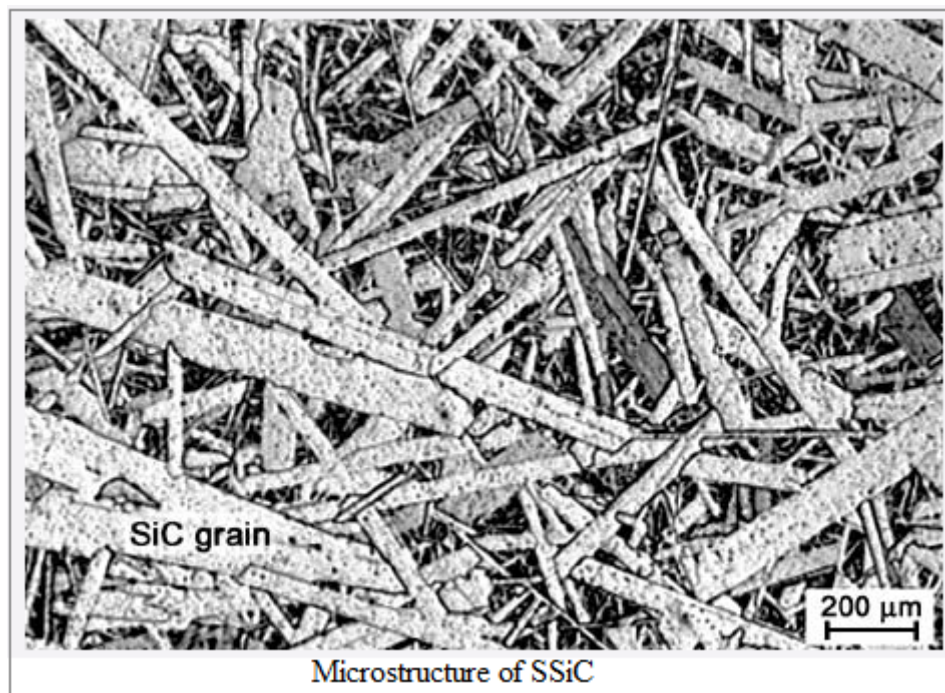


SiSiC is thus ideal as a material for highly stressed kiln furniture (beams, rolls, supports etc.) and various burner parts for direct and indirect combustion (flame tubes, recuperators and jet pipes). It is also useful in machine construction for components that must be highly resistant to wear and to corrosion.

- **Sintered silicon carbide (SSiC)**

It is produced using very fine SiC powder containing sintering additives. It is processed using forming methods typical for other ceramics and sintered at 2000 to 2200° C in an inert gas atmosphere. SSiC is distinguished by high strength that stays nearly constant up to very high temperatures (approximately 1600° C), maintaining that strength over long periods

This material displays an extremely high corrosion resistance in acidic and basic media, and this too is maintained up to very high temperatures. Thus, SSiC is ideal for extremely demanding applications, for example, slip ring seals in chemical pumps, bearing bushes, high temperature burner nozzles, or as kiln furniture for very high application temperatures.

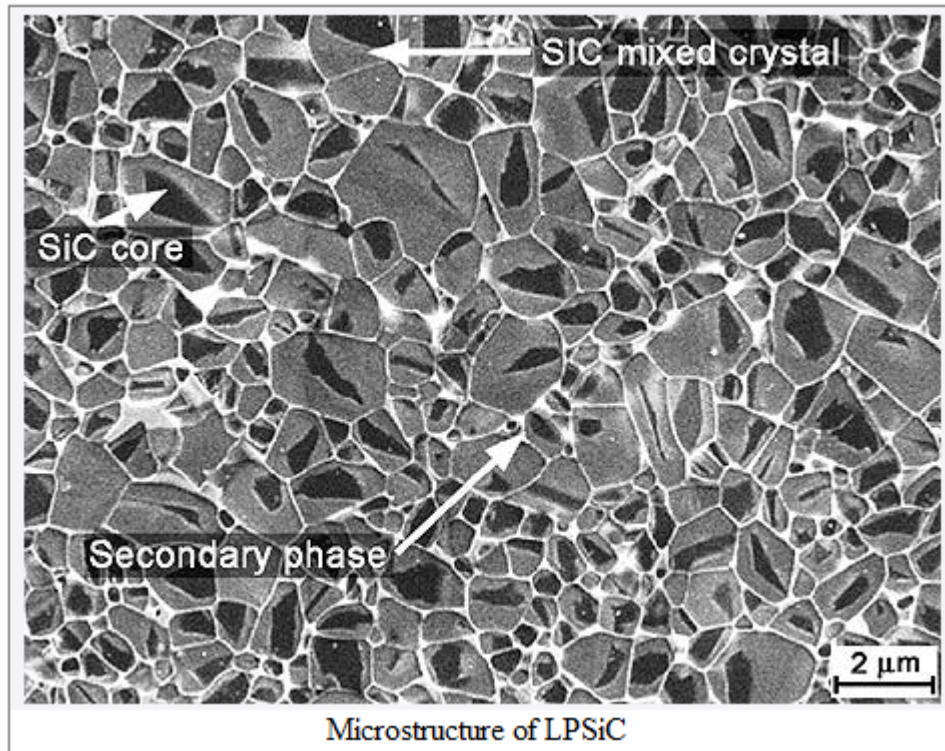


- **Hot pressed silicon carbide (HPSiC)**

It exhibits even better mechanical specifications compared to pressureless sintered SSiC, since the products are nearly free of pores due to the application of mechanical pressures reaching up to about 2000 bar. The axial pressing techniques limit the parts to be made to relatively simple or small geometries, and involve greater expense compared with pressureless sintering. As a result, HPSiC is used exclusively in the most demanding applications.

- **Liquid-phase sintered silicon carbide (LPSiC)**

It is a dense material containing SiC, a mixed oxynitride SiC phase, and an oxide secondary phase. The material is manufactured from silicon carbide powder and various mixtures of oxide ceramic powders. The oxide components are responsible here for the density which is somewhat higher than that of SSiC. The material is also characterised by very high strength and fracture toughness.



- **Examples of applications**

- Abrasives





- Burner nozzles



- Automotion

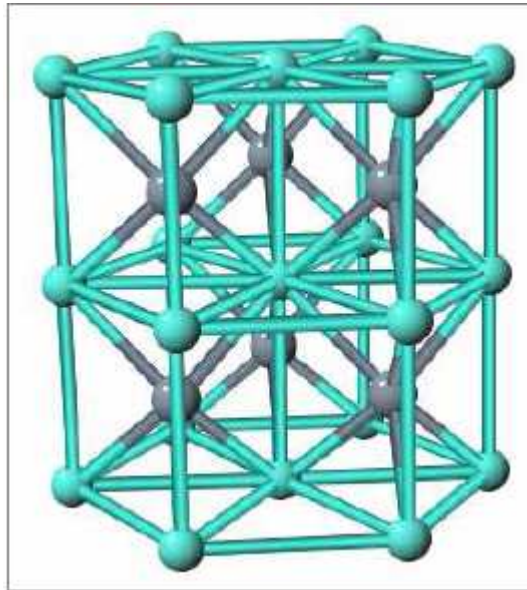


- Jewellery



➤ **Tungsten Carbide (WC)**

Tungsten Carbide is characterized by a hexagonal structure.



The main use of tungsten carbide is now in the manufacture of cemented carbide. Cemented carbide, or "hardmetal" as it is often called, is a material made by "cementing" very hard tungsten monocarbide (WC) grains in a binder matrix of tough cobalt metal by liquid phase sintering.

The combination of WC and metallic cobalt as a binder is a well-adjusted system not only with regard to its properties, but also to its sintering behaviour.

The high solubility of WC in cobalt at high temperatures and a very good wetting of WC by the liquid cobalt binder result in an excellent densification during liquid phase sintering and in a pore-free structure. As a result of this, a material is obtained which combines high strength, toughness and high hardness.

- **Applications**

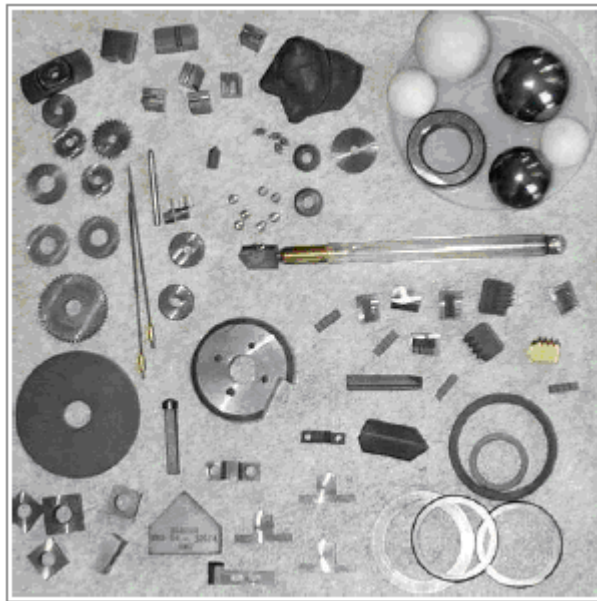
- **Cutting Tools**

Due to their high hardness and excellent impact resistance, cemented carbides are most commonly used for cutting tools in lathes and similar industrial machines.

Although cemented carbides are harder than the materials that they are generally used to machine they do wear. However, when the ceramic particles at the cutting face become dull, they either fracture or pull out of the metal matrix to expose fresh, sharp particles.



- Abrasive and wear resistance useful



- Other uses (sports, household, jewelry)



### 5.1.2.2 NITRIDES

#### ➤ Silicon Nitride (Si<sub>3</sub>N<sub>4</sub>)

Silicon Nitride (Si<sub>3</sub>N<sub>4</sub>) is the most important nitride ceramic. It plays at present a dominant role amongst nitride ceramics. It achieves a combination of outstanding material properties not yet reached by other ceramics, namely

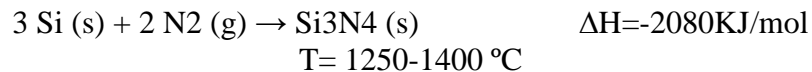
- High toughness,
- High strength, even at high temperatures,
- Outstanding thermal shock resistance,
- Remarkable resistance to wear,
- Low thermal expansion,
- Medium thermal conductivity and
- Good resistance to chemicals.

This combination of properties means that we have a ceramic that is appropriate for the toughest application conditions. Silicon nitride ceramics are therefore ideal for machine components with very high dynamic stresses and reliability requirements.

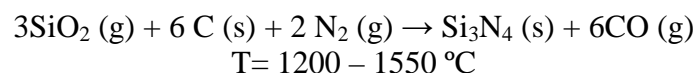
#### ● Synthesis of Si<sub>3</sub>N<sub>4</sub> powder

Si<sub>3</sub>N<sub>4</sub> does not exist in nature. There are three methods:

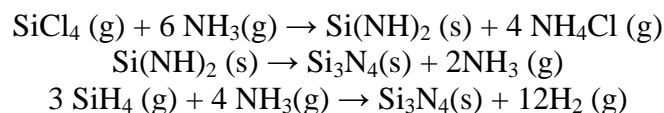
- Silicon powder nitriding



- Reduction of SiO<sub>2</sub> with C in N<sub>2</sub>



- Reaction between SiH<sub>4</sub> or SiCl<sub>4</sub> and NH<sub>3</sub> vapor

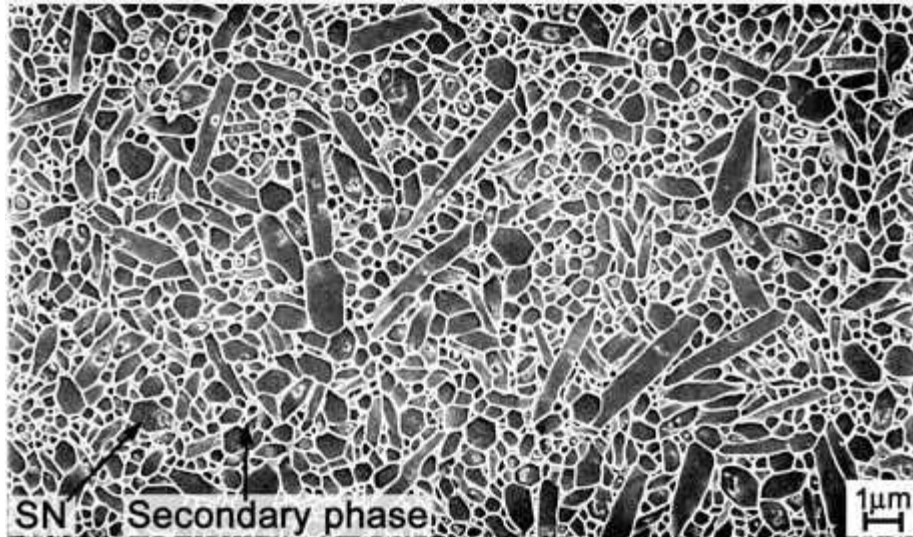


#### ● Low-pressure sintered silicon nitride(SSN)

A relatively economical version is that of SSN, which has medium bending strength, and from which high-volume components can be manufactured.

- **Gas pressure sintered silicon nitride (GPSSN)**

It is sintered in a gas pressure sintering furnace with an excess  $N_2$  pressure of up to 100 bar. This creates a high performance material suitable for high mechanical stresses.



- **Hot pressed silicon nitride (HPSN)**

It under go even higher pressures of up to 2000 bar during the sintering process. HPSN is distinguished by even greater mechanical strength, compared to GPSSN, because the remaining porosity is almost completely eliminated by the high mechanical pressures involved in the manufacturing process. The limited geometries available with axially pressed HPSN (due to the use of a mechanical pressing punch) is disadvantage associated with this ceramic.

Important fields of application for components made from this dense silicon nitride material are metal processing with cutting tools (indexable cutting inserts), roller bearing technology using balls, rollers or rings, and machine construction involving highly stressed machine elements.

- **Reaction bonded silicon nitride (RBSN)**

It is manufactured using a completely different approach. As an alternative to the high priced  $Si_3N_4$  powder, the relatively economical Si powder is used here as a raw material. The resulting ceramic displays good mechanical properties, but is prone to oxidation at high temperatures due to its very fine open porosity. It is only suitable for materials with thicknesses of up to 20 mm.

Examples of the application of RBSN include kiln furniture, melting crucibles and ingot moulds.

- **Applications**

- **Automotion Industry**



- **Aerospace industrial**



- **Chemical Industry**



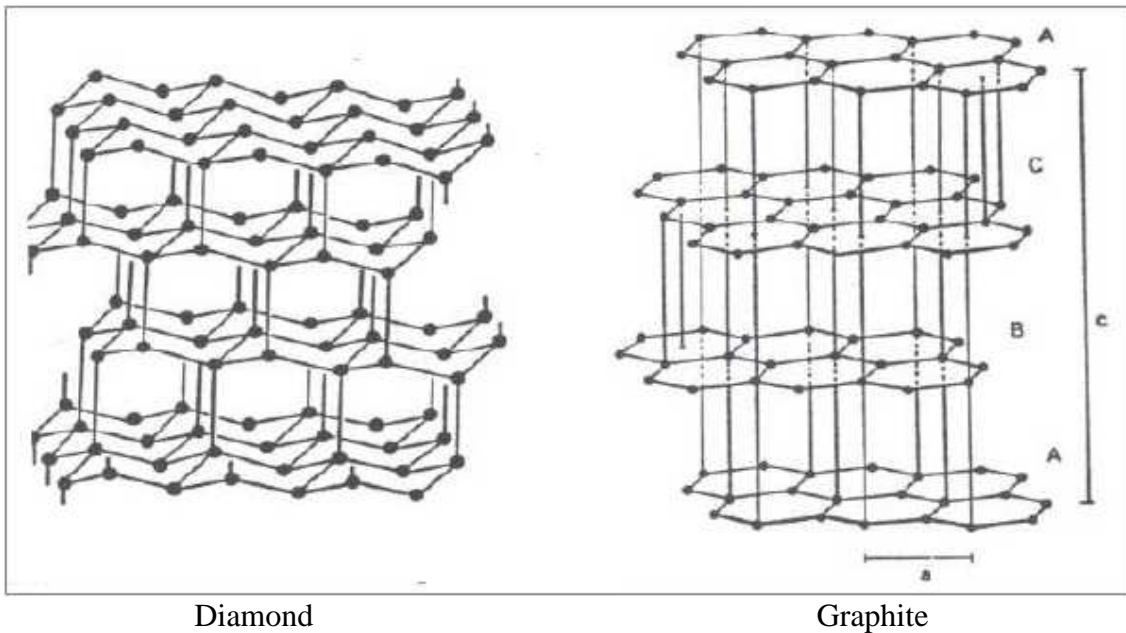
- **Industrial wear**





### 5.1.2.3 DIAMOND AND GRAPHITE

Carbon has two natural crystalline allotropic forms: graphite and diamond. Each has its own distinct crystal structure and properties.



#### ➤ GRAPHITE

The material is generally greyish-black, opaque and has a lustrous black sheen. It is unique in that it has properties of both a metal and a non-metal. It is flexible but not elastic, has a high thermal and electrical conductivity, and is highly refractory and chemically inert.

The unusual combination of properties is due to its crystal structure. The carbon atoms are arranged hexagonally in a planar condensed ring system. The layers are stacked parallel to each other. The atoms within the rings are bonded covalently, whilst the layers are loosely bonded together by van der Waals forces. The high degree of anisotropy in graphite results from the two types of bonding acting in different crystallographic directions. For example, graphite's ability to form a solid film lubricant comes from these two contrasting chemical bonds. The fact that weak Van der Waals forces govern the bonding between individual layers permits the layers to slide over one another making it an ideal lubricant.

There are two main classifications of graphite, natural and synthetic.

- Natural Graphite

Natural Graphite is a mineral consisting of graphitic carbon. It varies considerably in crystallinity. Most commercial (natural) graphites are mined and often contain other minerals. Natural graphite is an excellent conductor of heat and electricity. It is stable over a wide range of temperatures. Graphite is a highly refractory material with a high melting point (3650°C.)

Natural graphite is subdivided into three types of material:

- **Amorphous**

Amorphous graphite is the least graphitic of the natural graphites. However, the term "amorphous" is a misnomer since the material is still crystalline. Amorphous graphite is found as minute particles in beds of mesomorphic rocks such as coal or shale deposits.

- **Flake**

Flake graphite is found in metamorphic rocks uniformly distributed through the body of the ore or in concentrated lens shaped pockets. Flake graphite is removed by froth flotation.

- **High Crystalline**

Crystalline vein graphite is believed to originate from crude oil deposits that through time, temperature and pressure have converted to graphite. Vein graphite fissures are typically between 1cm and 1 m thick, and are typically > 90% pure.

- **Synthetic Graphite**

Synthetic graphite can be produced from coke and pitch. It tends to be of higher purity though not as crystalline as natural graphite. There are essentially two types of synthetic graphite. The first is electrographite, which is pure carbon produced from calcined petroleum coke and coal tar pitch in an electric furnace. The second type of synthetic graphite is produced by heating calcined petroleum pitch to 2800°C. On the whole synthetic graphite tends to be of a lower density, higher porosity and higher electrical resistance. Its increased porosity makes it unsuitable for refractory applications.

- **Applications**

- **Refractory Materials**

Due to its high temperature stability and chemical inertness graphite is a good candidate for a refractory material. It is used in the production of refractory bricks. Graphite is also used to manufacture crucibles, ladles and moulds for containing molten metals.

The electrodes used in many electrical metallurgical furnaces are manufactured from graphite such as the electric arc furnaces used for processing steel.

- **Nuclear Industry**

High purity electrographite is used in large amounts for the production of moderator rods and reflector components in nuclear reactors. Their suitability arises from their low absorption of neutrons, high thermal conductivity and their high strength at temperature.

- **Chemical Industry**
- **Electrical Applications**
- **Mechanical Applications**
- **Lubricant**



## ➤ **DIAMOND**

Diamond is a crystalline, transparent and extremely hard allotrope of carbon having a tetrahedral structure of carbon atoms with strong.

### ● **Properties**

Diamond provides an impressive combination of chemical, physical and mechanical properties:

- The hardest known material
- Low coefficient of friction
- High thermal conductivity
- High electrical resistivity
- Low thermal expansion coefficient
- High strength
- Broad optical transparency from ultra violet to infra red
- Resistant to chemical corrosion
- Biologically compatible

### ● **Sources and Processing**

Diamond can now be found from several sources:

- Naturally occurring diamond; about 20 tonnes of diamond are mined each year. Half are gem quality and half are industrial quality.
- Synthetic single crystal diamond:

- High-pressure and high temperature (HPHT):

About 90 tonnes of diamond are made annually by the high-pressure and high temperature (HPHT) method. Most industrial diamond is made from graphite at pressures of 4.5 to 6.0 GPa and temperatures of 1400 to 1600°C with the aid of a molten transition metal catalyst. These diamonds are considerably cheaper than natural diamond.

- Vapour phase deposition:
    - Chemical vapour deposition (CVD)
    - Physical vapour deposition (PVD)

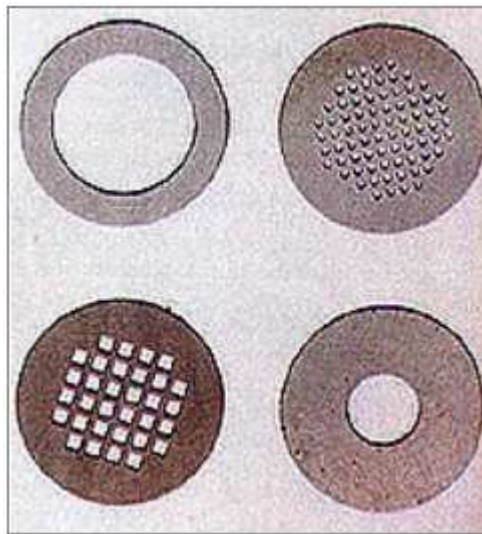
Both chemical vapour deposition (CVD) and physical vapour phase deposition (PVD) produce thin diamond films. About 10 tonnes of vapour phase grown diamond films are produced annually. Their cost is more than four times that of naturally occurring diamond. However, their application can be justified economically as they are used in thin film form and make a significant difference to component properties.

- **Chemical Vapour Deposition (CVD)**

Polycrystalline diamond can be grown by a number of different CVD techniques:

- **Microwave Plasma Assisted Chemical Vapour Deposition**

It is used for growing free-standing diamond, typically between 50 $\mu$ m and 2000 $\mu$ m thick, and for growing coatings (<50 $\mu$ m thick), which can cover structures up to 200 mm in diameter. For self-supporting material the polycrystalline diamond is usually grown on silicon substrates, which are chemically removed after growth. The wafers can then be polished, processed and laser cut to the required device dimensions.



Diamond grids

- **Hot filament deposition**

The hot filament chemical vapour deposition system was specially built for producing thick, adherent and coherent poly-crystalline diamond films on metallic and ceramic substrates.

The deposited poly-crystalline layers have a substantially uniform micro-structure, with high electrical resistivity.

The equipment is designed for depositing multi-layer poly-crystalline diamond films, which have a wide use in electronic industries.

- **Plasma jet deposition**

This method enables the synthesis of a diamond film of unlimited thickness applied to very large areas. The plasma jet technology produces a diamond deposit of exceptional purity and greatest deposition rate compared to other existing CVD methods.

- **Combustion flame deposition**

A precursor compound, usually a metal-organic compound or a metal salt, is added to the burning gas. The flame is moved closely above the surface to be coated. The high energy within the flame converts the precursors into highly reactive intermediates, which readily react with the substrate, forming a firmly adhering deposit. The microstructure and thickness of the deposited layer can be controlled by varying process parameters such as speed of substrate or flame, number of passes, substrate temperature and distance between flame and substrate.

- **Applications**

- **Cutting Tools and Wear Components**

The properties exploited by these applications are hardness, strength, low thermal expansion coefficient, low friction coefficient and chemical resistivity.



- **Thermal Management in Substrates, Heat Spreaders and Heat Sinks**

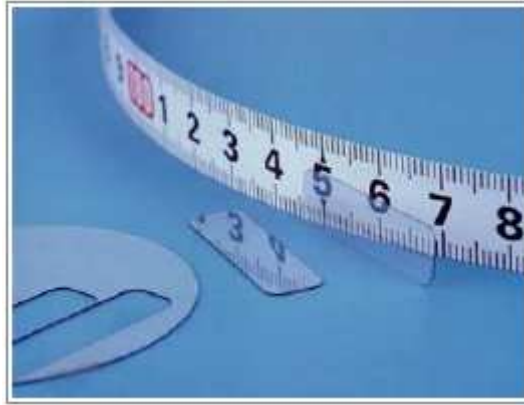
Diamond provides the unique combination of high thermal conductivity with electrical insulation.

- **Semiconductor devices**

Potential applications include very high power transistors, high temperature integrated circuits, piezoelectric devices and radiation hardened integrated circuits.

- **Optical components**

Diamond is starting to be used in optical components, particularly as a protective coating for infrared optics in harsh environments. A thin layer of CVD diamond can protect Infra Red windows made from ZnS, ZnSe, and Ge, which are brittle and easily damaged.



- **High Performance Applications**
- **Gemology**



## **5.2 FUNCTIONAL CERAMICS**

### **5.2.1 FAST ION CONDUCTORS**

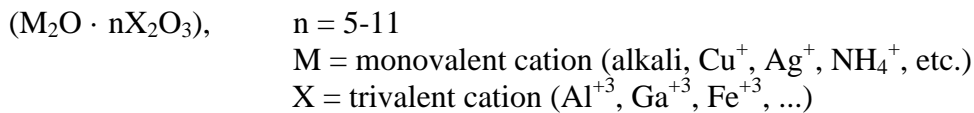
In solid-state ionics, fast ion conductors, also known as solid electrolytes and superionic conductors, are materials that act as solid state ion conductors and are used primarily in solid oxide fuel cells. As solid electrolytes they conduct due to the movement of ions through voids, or empty crystallographic positions, in their crystal lattice structure. The most commonly used solid electrolyte is yttria stabilized zirconia. One component of the structure, the cation or anion, is essentially free to move throughout the structure, acting as charge carrier.

Fast ion conductors are intermediate in nature between crystalline solids which possess a regular structure with immobile ions, and liquid electrolytes which have no regular structure and fully mobile ions. Solid electrolytes find use in all solid state supercapacitors, batteries and fuel cells, and in various kinds of chemical sensors.

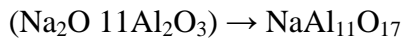
Examples: the most important examples of fast ion conductors are:

- $\beta$ -alumina solid electrolyte
- Zirconium dioxide ( $\text{ZrO}_2$ )
- Silver (Ag)

- **$\beta$ -alumina solid electrolyte**



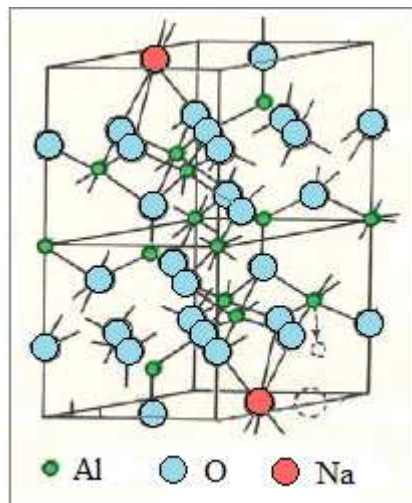
It's important to know: sodium  $\beta$ -alumina (M = Na + and X =  $\text{Al}^{3+}$ ). Sodium is which provide the best properties.



There are different varieties:

- $\beta$ :  $n = 8-11$ ,
- $\beta''$ :  $n = 5-7$  (rich in sodium) more conductive ( $\text{M}_2\text{O} \cdot 5-6 \text{X}_2\text{O}_3$ )

Structure defined in layers: compacted layers of  $\text{O}^{2-}$ , but every fifth layer is missing three quarters of oxygen.  $\text{Na}^+$  occupy these positions in the oxygen-deficient layer. The other four layers are occupied by  $\text{Al}^{3+}$  in the octahedral and tetrahedral positions.



- **Zirconium dioxide ( $\text{ZrO}_2$ )**

Advantages:

- It is refractory ( $1500^\circ \text{C}$ )
- Very good oxygen ionic conductor

Disadvantages:

- It's not as good ionic conductor as the electrolyte of sodium and silver.

- **Silver (Ag)**

AgI is the best conductor, and it is characterized by:

- Low ion charge:  $\text{Ag}^+$
- Low coordination during movement
- Highly polarizable anion:  $\text{I}^-$
- Very high number of empty positions

- **Applications**

- **Batteries**

Devices capable of storing energy. Classification:

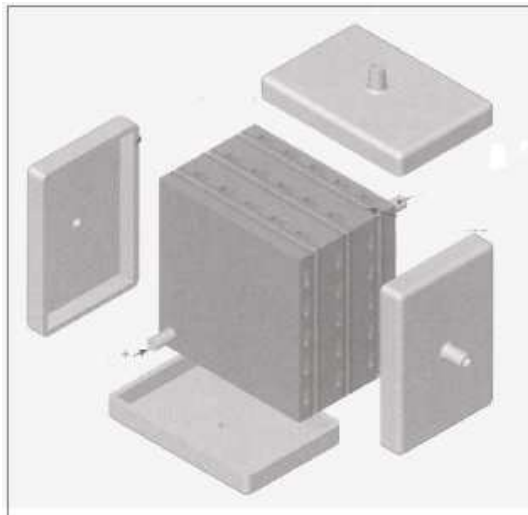
Primary Batteries: No rechargeable small, with long lifetime and not to download during this period. Low cost, no maintenance.

Example: Zn-carbon battery, Li, alkaline

Secondary batteries: rechargeable high energy density. Small size, with a time of solid electrolytes in electrochemical devices the solid state.

Example: Pb-acid batteries, Ni-Cd, Ni-MH, Na-S, Li-Ion

- **Fuel Cells**



- **Electrochemical sensors**

- **Electrochromic Devices**



### 5.2.2 SUPERCONDUCTORS

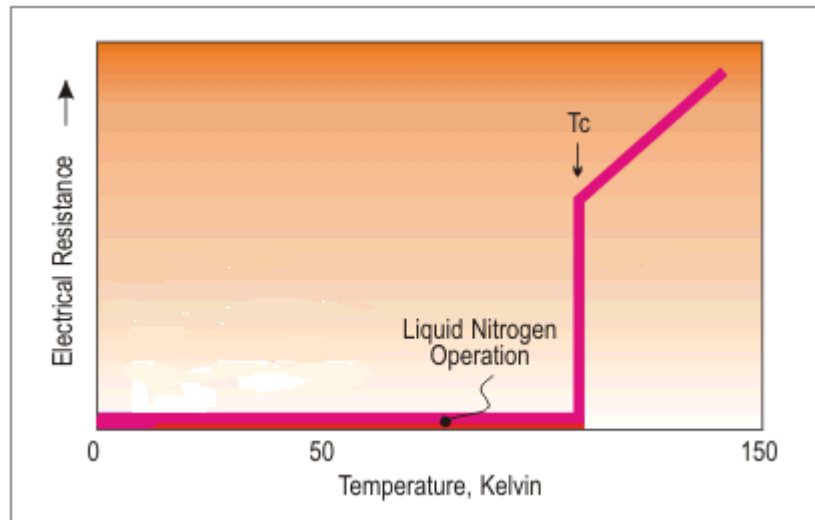
Superconductors are a class of compounds which conduct electricity without resistance and are impermeable to magnetic flux below a critical temperature. As a result of this, they are ubiquitous in applications as diverse as MRI scanners, Earth-orbiting deep space cameras and Maglev trains.



- **Characteristics of a superconductor**

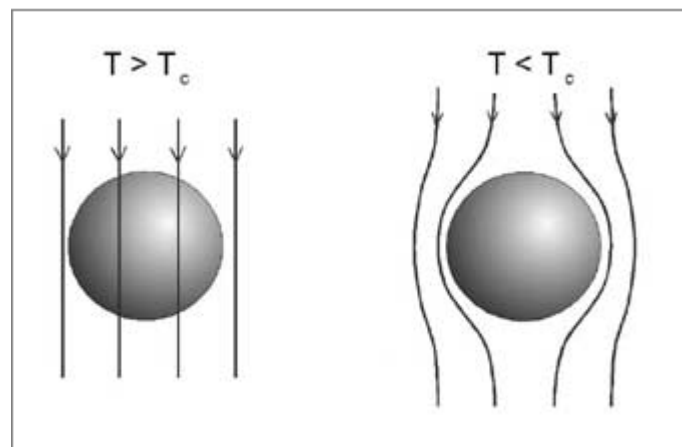
- **Zero resistance**

Superconductors lose all resistance to the flow of direct electrical current and nearly all resistance to the flow of alternating current when cooled below a critical temperature, which is different for each superconducting material.



- **Perfect Conductor of Electricity**

A superconductor is a perfect conductor of electricity; it carries direct current with 100% efficiency because no energy is dissipated by resistive heating. Once induced in a superconducting loop, direct current can flow undiminished forever. Superconductors also conduct alternating current, but with some slight dissipation of energy. It is a perfect diamagnetic,  $\chi = -1$





- **Types of superconductors**

Metals	T <sub>c</sub> [K]
Nb	9,15
V	5,3
Ta	4,48
Ti	0,39
Sn	3,72
Intermetallic	T <sub>c</sub> [K]
Nb <sub>3</sub> Ge	23,2
Nb <sub>3</sub> Sn	21
Nb <sub>3</sub> Al	17,5
NbTi	9,5
Ceramic	T <sub>c</sub> [K]
Tl <sub>2</sub> Ba <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>x</sub>	122
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	90
Ba <sub>1-x</sub> K <sub>x</sub> BiO <sub>3-γ</sub>	30

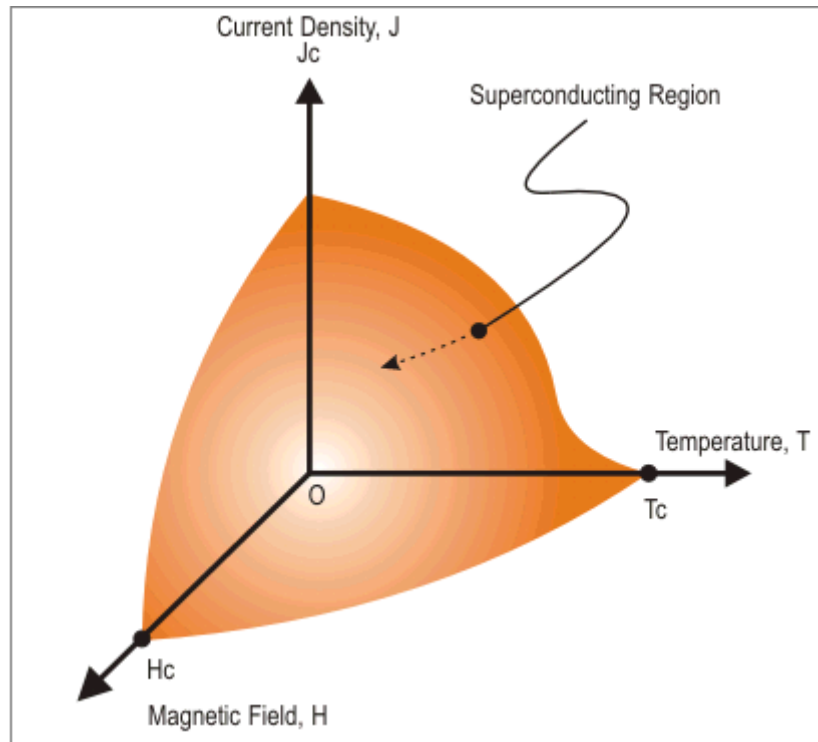
Metal: T<sub>c</sub> = 0-10 K

Intermetallic: T<sub>c</sub> = 10-25 K

Ceramic: T<sub>c</sub> = 30-150 K

- **Critical parameters**

- The material must be cooled below a characteristic temperature, known as its critical temperature (**T<sub>c</sub>**).
- The current passing through a given cross-section of the material must be below a characteristic level known as the critical current density (**J<sub>c</sub>**).
- The magnetic field to which the material is exposed must be below a characteristic value known as the critical magnetic field (**H<sub>c</sub>**).



- **Classification**

- Type I

This category of superconductors is mainly comprised of metals that show some conductivity at room temperature. They require incredible cold to slow down molecular vibrations sufficiently to facilitate unimpeded electron flow.

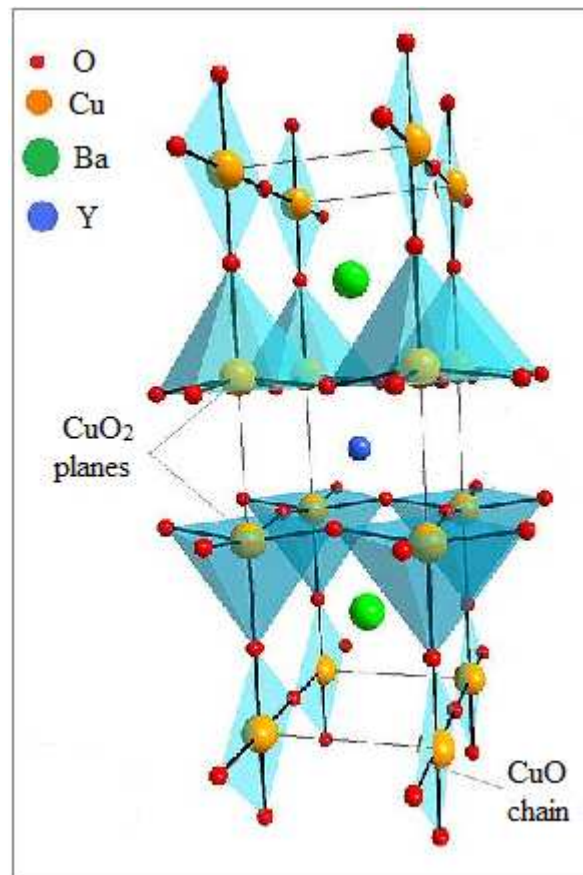
- Type II

The type II category is comprised of transition metal elements (Nb, V,  $Nb_3Ge$ ,  $Ni_3Sb$ ,  $YBaCuO...$ ). It is characterized by having superior  $T_c$  and  $H_c$ .

- **YBaCuO superconductors**

The structure of a high- $T_c$  superconductor is closely related to perovskite structure, and the structure of these compounds has been described as a distorted, oxygen deficient multi-layered perovskite structure. One of the properties of the crystal structure of oxide superconductors is an alternating multi-layer of  $CuO_2$  planes with superconductivity taking place between these layers. The more layers of  $CuO_2$  the higher  $T_c$ .

$YBa_2Cu_3O_{7-x}$  was the first superconductor found with  $T_c > 77$  K (liquid nitrogen boiling point). The unit cell of  $YBa_2Cu_3O_7$  consists of three pseudocubic elementary perovskite unit cells. Each perovskite unit cell contains a Y or Ba atom at the center: Ba in the bottom unit cell, Y in the middle one, and Ba in the top unit cell.



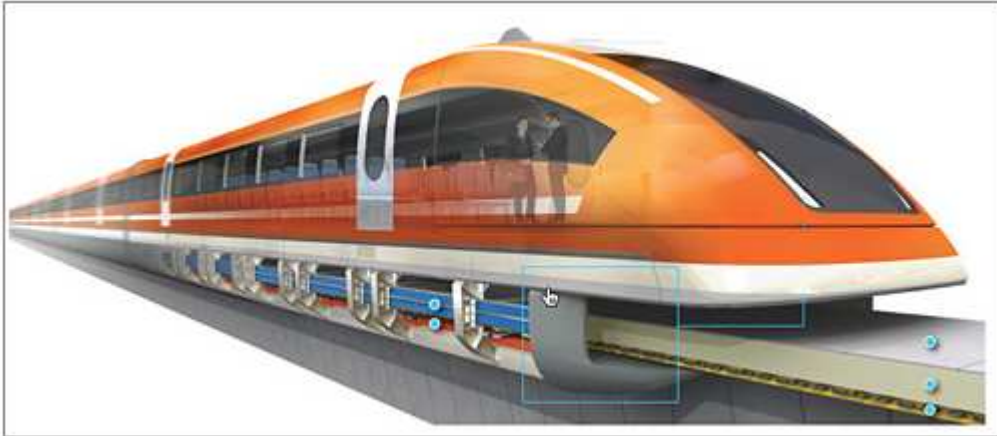
Superconductivity is caused by the presence of Cu-O layers located between planes of other elements. Superconductivity occurs in these planes, where the elements present and the distances between the planes change the superconducting transition temperature.

- **Applications**

Possible applications are based on the absence of electrical resistance, the ability to create superconducting magnets, the Meissner effect (levitation, the expulsion of a magnetic field from a superconductor) and the Josephson effect (a current that flows indefinitely long without any voltage applied).

- **Maglev trains**

Maglev, is a system of transportation that uses magnetic levitation to suspend, guide and propel vehicles from magnets rather than using mechanical methods, such as wheels, axles and bearings. Maglev transport is a means of flying a vehicle or object along a guideway by using magnets to create both lift and thrust, only a few inches above the guideway surface. High-speed maglev vehicles are lifted off their guideway and thus are claimed to move more smoothly and quietly and require less maintenance than wheeled mass transit systems – regardless of speed.



- **Superconducting magnet**

It is an electromagnet made from coils of superconducting wire ( $\text{NbTi}$  or  $\text{Nb}_3\text{Sn}$ ). They must be cooled to cryogenic temperatures during operation. In its superconducting state the wire can conduct much larger electric currents than ordinary wire, creating intense magnetic fields. Superconducting magnets can produce greater magnetic fields than all but the strongest electromagnets and can be cheaper to operate because no energy is dissipated as heat in the windings.

- **Generators**

They produce energy by spinning a magnet inside the other. They are made with low-temperature magnets, so they are efficient and cheap. You save only 1% of energy, so it does not compensate its research, they don't exist in operation.

- **Electric power transmission**

High-temperature superconductors promise to revolutionize power distribution by providing lossless transmission of electrical power compared with losses of 5 and 8% of Cu and Al wires.

Superconducting cables are particularly suited to high load density areas such as the business district of large cities, where purchase of an easement for cables would be very costly

- **Superconducting quantum interference devices (SQUID)**

Superconductors are used to build Josephson junctions which are the building blocks of SQUIDs, the most sensitive magnetometers known. SQUIDs are used in scanning SQUID microscopes and magnetoencephalography.

### 5.2.3 FERRITES

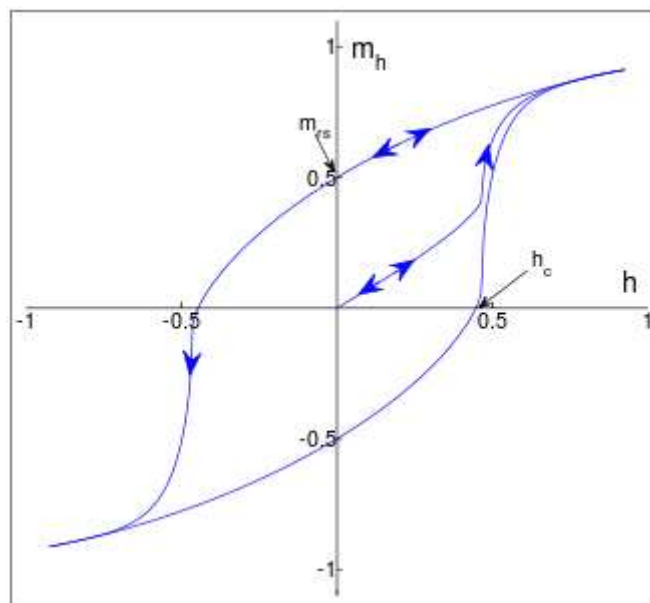
Ferrites are chemical compounds consisting of ceramic materials with Fe (III) oxide ( $\text{Fe}_2\text{O}_3$ ) as their principal component. Many of them are magnetic materials and they are used to make permanent magnets, ferrite cores for transformers, and in various other applications.

- **Types of magnetism**

- Diamagnetic: the atoms haven't magnetic moment
- Paramagnetic: the atoms have magnetic moment randomly oriented
- Ferromagnetic: atoms with magnetic moments aligned and parallel
- Antiferromagnetic: atoms with antiparallel magnetic moments
- Ferrimagnetic: atoms with antiparallel and parallel magnetic moments

- **Hysteresis**

When an external magnetic field is applied to a ferromagnet such as iron, the atomic dipoles align themselves with it. Even when the field is removed, part of the alignment will be retained: the material has become magnetized. Once magnetized, the magnet will stay magnetized indefinitely. To demagnetize it requires heat or a magnetic field in the opposite direction.



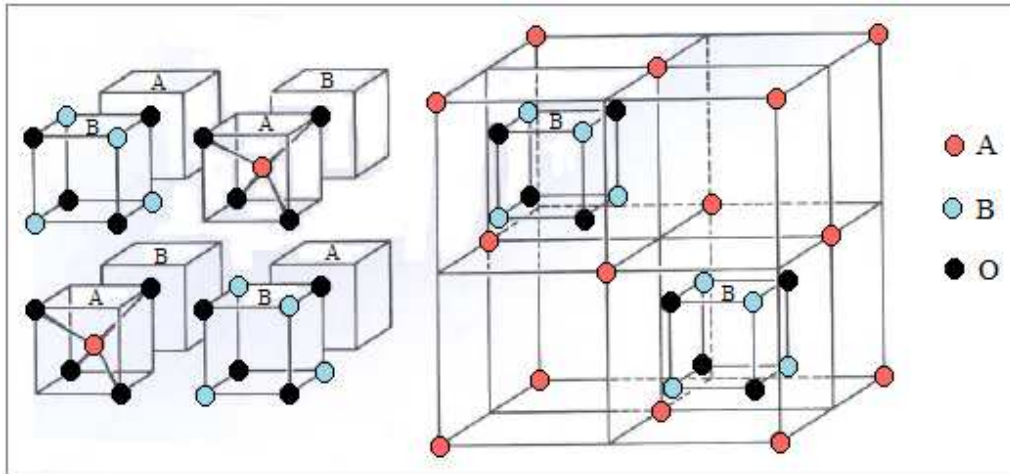
Plot of magnetization  $m$  against magnetic field  $h$

Ferrites are usually non-conductive ferrimagnetic ceramic compounds derived from iron oxides such as hematite ( $\text{Fe}_2\text{O}_3$ ) or magnetite ( $\text{Fe}_3\text{O}_4$ ) as well as oxides of other metals. Ferrites are, like most other ceramics, hard and brittle. In terms of their magnetic properties, the different ferrites are often classified as "soft" or "hard", which refers to their low or high magnetic coercivity.

- **Soft Ferrites (Spinel)**

- Structure

It has the structure of the spinel ( $AB_2O_4$ ):

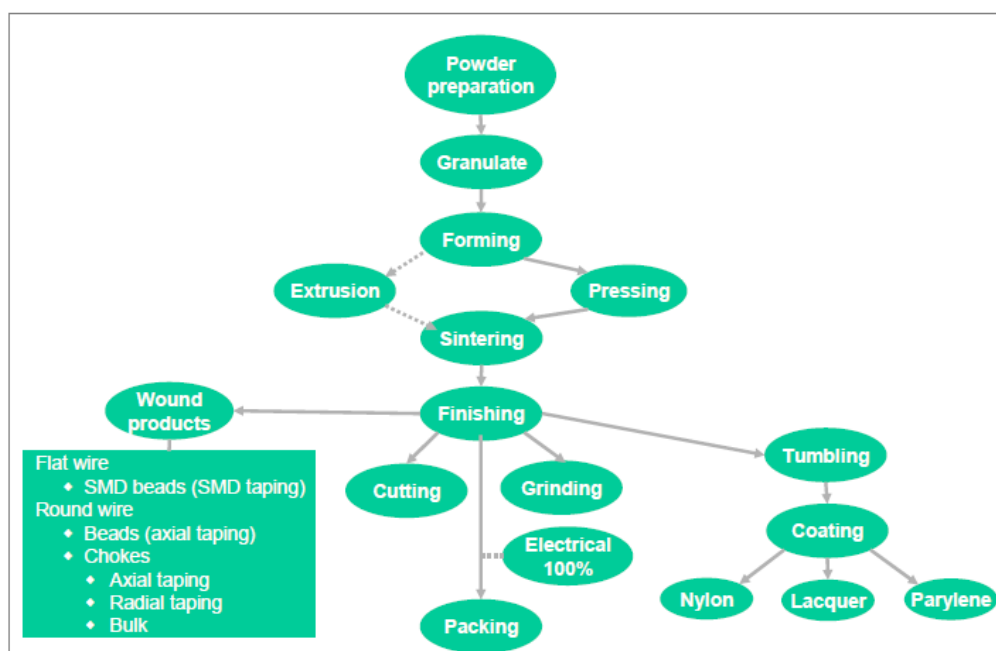


The spinels are ferromagnetic

The most common soft ferrites are:

- Manganese-zinc ferrite,  $MnZn$ , with the formula  $Mn_xZn_{1-x}(Fe_2O_4)$ :  $MnZn$  have higher permeability and saturation induction than  $NiZn$ .
- Nickel-zinc ferrite,  $NiZn$ , with the formula  $Ni_xZn_{1-x}(Fe_2O_4)$ :  $NiZn$  ferrites exhibit higher resistivity than  $MnZn$ , and are therefore more suitable for frequencies above 1 MHz.

- **Production**



- **Applications**

- **Ferrite bead**

A ferrite bead is a passive electric component used to suppress high frequency noise in electronic circuits.



- **Electronic inductors**

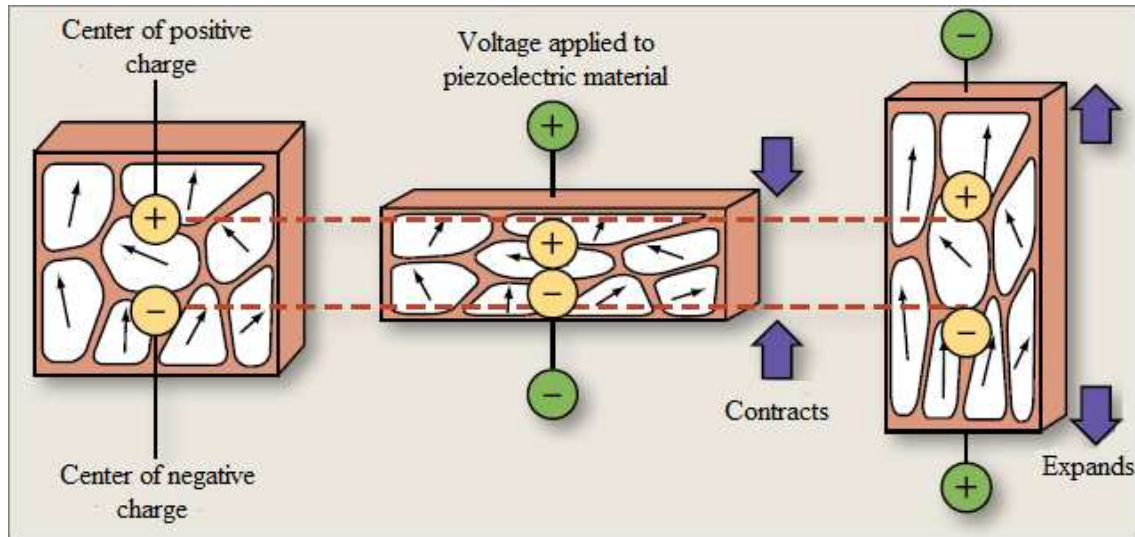
For inductor cores soft ferrites are used, which have low coercivity and thus low hysteresis losses

- **Electronic amplifiers**

An amplifier is a device for increasing the power of a signal by use of an external energy source.

### 5.2.4 PIEZOELECTRICS

A piezoelectric substance is one that produces an electric charge when a mechanical stress is applied. Conversely, a mechanical deformation is produced when an electric field is applied. The electrical response to mechanical stimulation is called the direct piezoelectric effect and the mechanical response to electrical stimulation is called the converse piezoelectric effect.



- **Principles**

The piezoelectricity of ferroelectric materials is a consequence of the existence of polar areas (domains) whose orientation changes as result of the polarisation, namely of the application of an electrical voltage. The polarisation is associated with a change in length,  $\Delta S$ .

- **Structure of Piezoelectric Crystals**

Piezoelectricity is the property of nearly all materials that have a non-centrosymmetric crystal structure. Some naturally occurring crystalline materials possessing these properties are quartz and tourmaline. Some artificially produced piezoelectric crystals are Rochelle salt ( $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ), ammonium dihydrogen phosphate and lithium sulphate. Another class of materials possessing these properties is polarized piezoelectric ceramic. In contrast to the naturally occurring piezoelectric crystals, piezoelectric ceramics are of a polycrystalline structure.

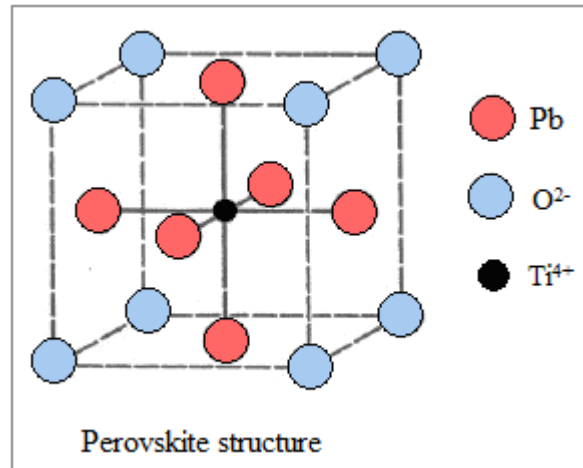
- **Lead zirconate titanate (PZT)**

Currently the most important piezoelectric ceramic materials are based on mixed oxide crystal system consisting of lead zirconate and lead titanate known as lead zirconate titanate (PZT).



The specific properties of these ceramics, such as the high dielectric constant, are dependent on the molar ratio of lead zirconate to lead titanate as well as on substitution and doping with additional elements. A wide range of modifications can be implemented in this way, creating materials with highly varied specifications.

PZT (and many other piezoelectric materials) have crystal structures belonging to the perovskite family with the general formula  $ABO_3$ .



Before poling, a piezoelectric ceramic material consists of small grains, each containing domains in which the polar direction of the unit cells are aligned. These grains and domains are randomly oriented, hence the net polarization of the material is zero, namely the ceramic does not exhibit piezoelectric properties. The application of a sufficiently high DC field (called poling process) will orient the domains in the field direction and lead to a remanent polarization of the material.

- **Applications**

- **High voltage and power sources**

Direct piezoelectricity of some substances like quartz, can generate potential differences of thousands of volts.

- **Sensors**

Piezoelectric sensors have proven to be versatile tools for the measurement of various processes. They are used for quality assurance, process control and for research and development in many different industries. It has been successfully used in various applications, such as in medical, aerospace, nuclear instrumentation, and as a pressure sensor in the touch pads of mobile phones. In the automotive industry, piezoelectric elements are used to monitor combustion when developing internal combustion engines. The sensors are either directly mounted into additional holes into the cylinder head or the spark/glow plug is equipped with a built in miniature piezoelectric sensor.

- **Actuators**

As very high electric fields correspond to only tiny changes in the width of the crystal, this width can be changed with better-than- $\mu\text{m}$  precision, making piezo crystals the most important tool for positioning objects with extreme accuracy — thus their use in actuators.

- **Buzzers**

A piezoelectric element may be driven by an oscillating electronic circuit or other audio signal source, driven with a piezoelectric audio amplifier. Sounds commonly used to indicate that a button has been pressed are a click, a ring or a beep.



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