INTRODUCTION TO CERAMICS, GLASS AND REFRACTORIES

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4) Raw Materials

Natural Occurring Minerals &
Traditional Ceramics

"You're fired."

Synthetic Minerals &
Technical Ceramics

Naturally Occurring Minerals•

Minerals are the constituents of rocks, rocks are usually not composed of a single mineral; rather they are an aggregate of two or more minerals.

Igneous Rocks are formed by cooling and solidification of magma.

Metamorphic Rocks have undergone structural and/or chemical transitions.

Sedimentary Rocks are formed when smaller particles become cemented.

Most minerals need to go through some form of physical or chemical processing before use. Physical beneficiation process includes crushing and grinding of coarse rocks. The particle size of the raw material may affect subsequent steps in the production process. An example that we use is producing alumina Al_2O_3 from bauxite, a process that involves a chemical reaction

IRAQI MINERALS:

Dolamite $MgCO_3.CaCO_3$: الانبار،الحسينيات، الرطبة وايظا في الغضاري في السماوة

Limestone $CaCO_3$: حزام طولي من حجر الكلس من هيت الى السلمان

Bentonite – Ca-montmorillonitic Clay: الانبار

Gypsum: من القائم على طول نهر الفرات الى هيت

Phosphate Rocks: عكاشات والحدود العراقية الاردنية

Bauxite – Crust Bauxite and Bauxite claystone: الانبار

Iron Stone: الحسينيات

Feldspathic sand, silica sand containing up to 20% Feldspar: النجف

Red Kaolinite – red high elasticity rich in Iron: الحسينيات

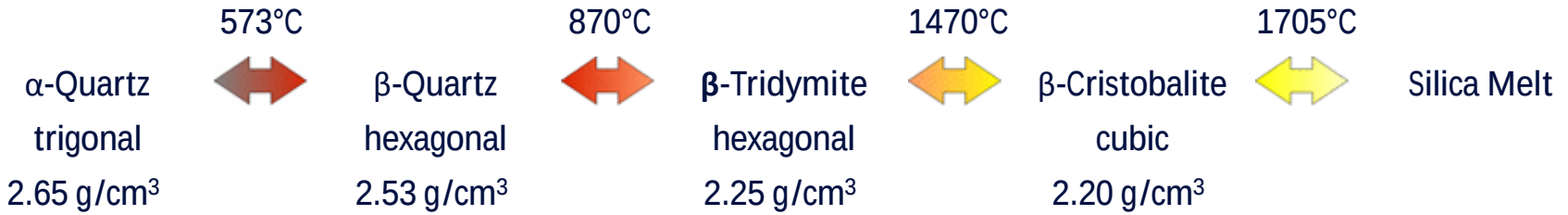
Kaolin $Al_2O_3.2SiO_2.2H_2O$: المنطقة الغربية – دويخلة – السمحات

There are so many other minerals that you can refer to in the text books,

Furthermore several important ceramics do not occur naturally in mineral form and must be fabricated chemically. Synthesis of ceramic powders can have advantages not only in purity but also in allowing the generation of fine particle sized powders having a well-defined morphology

Silicates

The silicates are the largest, the most interesting and the most complicated class of minerals than any other minerals. Approximately 30% of all minerals are silicates and some geologists estimate that 90% of the Earth's crust is made up of silicates, SiO_4^{4-} based material. Thus, oxygen and silicon are the two most abundant elements in the earth's crust. Of all silica polymorphs, **quartz is the only stable form** at normal ambient conditions, and all other silica polymorphs will - given sufficient time - eventually transform into quartz. The other polymorphs are stable at different and sometimes very special conditions, mostly high temperatures and high pressures, but some of them may also form at low temperatures and pressures under conditions where quartz is stable.



Volume change associated with polymorphic transformation limits application of cristobalite and quartz. A small addition of $CaCo_3$ or CaO at firing temperature precipitate SiO_2 as tridymite which has lower shrinkage during transformation and less likely to fracture or weakening refractory brick.

Fused Silica: high purity quartz melted at 2000°C, it has low thermal expansion and one of the best thermal shock ceramic materials

Clays

•Kaolin, China clay Al_2O_3•$2SiO_2$•$2H_2O$: pure, low plasticity, white burning clay

•Ball Clay: High plasticity, high green strength, dark in the unfired stage and burn white or creamy colour

•Fire Clay: All clays that are not white burning, use to make refractories and mortars

Mica

The mica group consists of 37 minerals, known as phyllosilicates, which have a layered or platy texture. True micas contain univalent cations (e.g., Na+ or K+) between each set of layers and show perfect basal cleavage, allowing the crystals to be split into thin sheets. The cleavage flakes are flexible and elastic

Mullite

Mullite (3Al2O3 · 2SiO2) does not exist in nature in large quantities and must be produced synthetically. It has many properties that make it suitable for high-temperature applications. It does not react readily with molten glass or with molten metal slags and is stable in the corrosive furnace atmosphere. Sintered mullite may be obtained from a mixture of kyanite (Al2OSiO4), a naturally occurring mineral found in metamorphic rocks, bauxite, and kaolin. This mixture (in the correct ratio) is sintered at temperatures up to about 1600^{o}C.

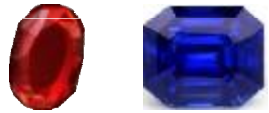
Synthetic Minerals - Technical Ceramics Raw Materials

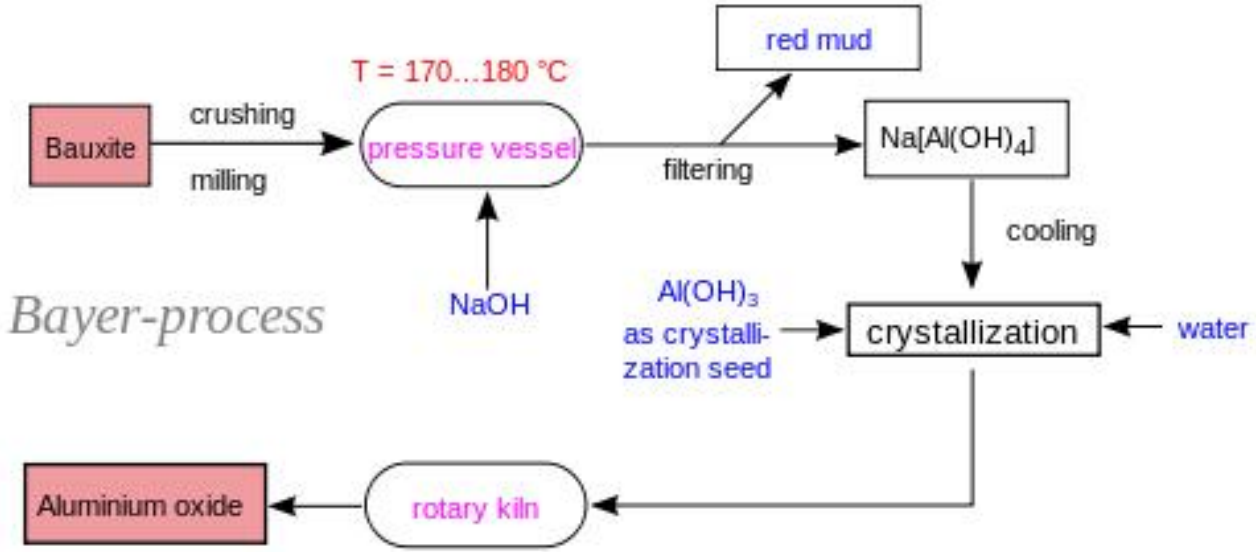
Advanced ceramics require a much higher quality and purity of raw materials, as well as the careful control of processing conditions and of the materials microstructure

Oxides

Alumina

Aluminum oxide (Al2O3, alumina, occurs naturally as corundum, Saphire and Ruby) is the most widely used inorganic chemical for ceramics and is produced from the mineral bauxite using the Bayer process. Polycrystalline alumina is being used in a wide range of applications because of its high strength, hardness, wear resistance and chemical inertness.





Magnesia

Magnesium oxide (MgO, magnesia) occurs naturally as the mineral periclase. The principal commercial sources of MgO are magnesite (MgCO3) and magnesium hydroxide [Mg(OH)2].

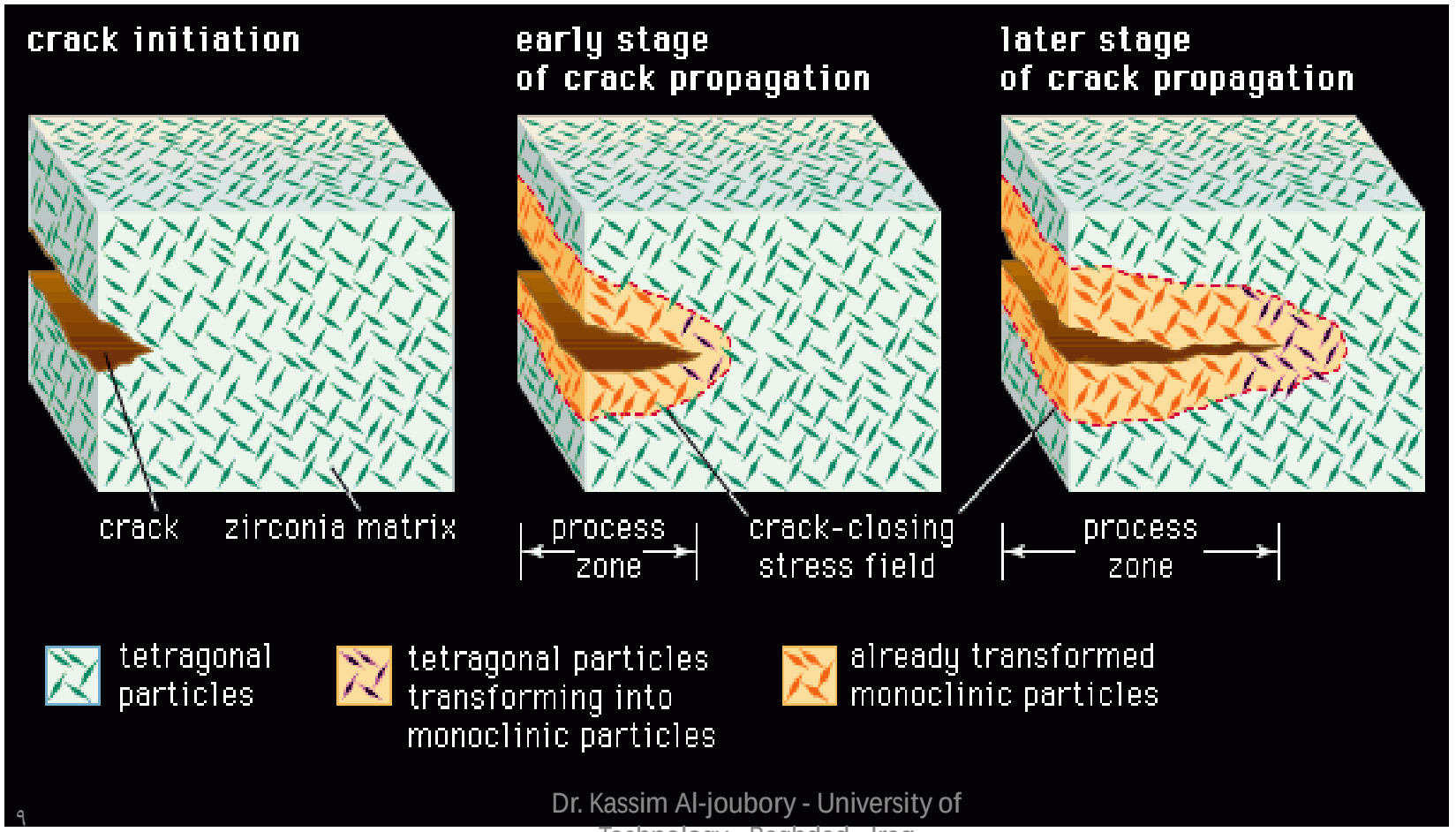
Magnesia is used as a basic refractory material and only attacked by acidic materials. Fully dense fine-grained, defect-free MgO, exhibit excellent mechanical, thermal, and optical properties.

Zirconia

Zirconium dioxide (ZrO_2, Zirconia) is principally derived from zircon, $ZrSiO_4$. It is a very important engineering ceramic material and has three phases : monoclinic < ١١٧٠ °C, tetragonal ١١٧٠°C-٢٣٧٠ °C, and cubic >٢٣٧٠ °C. The volume expansion caused by the cubic to tetragonal to monoclinic transformation induces large stresses, and these stresses cause ZrO_2 to crack upon cooling from high temperatures. When the zirconia is blended with some other oxides, the tetragonal and/or cubic phases are stabilized. Effective dopants include magnesium oxide (MgO), yttrium oxide (Y_2O_3, yttria), calcium oxide (CaO), and cerium(III) oxide (Ce_2O_3). Stabilized zirconia has superior thermal, mechanical, and electrical properties. Tetragonal zirconia is a very tough material where a stress concentration at a crack tip can cause the tetragonal phase to transform into monoclinic with an increase in volume. This phase transformation can then put the crack into compression, retarding its growth. This mechanism is knowing as transformation toughining .

Cubic Zirconia

Transformation Toughining



Titania (TiO_2)

Titanium dioxide occurs in nature as well-known minerals rutile, anatase and brookite. Titania is also produced by reacting ilmenite $FeTiO_3$ with sulfuric acid at 150–180°C followed by few processes and final calcinations at about 1000°C to produce titania TiO_2. Titania is widely used in pigments, coatings and component of sunscreens. Recently, it has attracted increasing attention in the electronics industry due to its high dielectric and semi-conducting properties, photocatalytic activity, and good biocompatibility

Non-oxide Ceramics

The non-oxide ceramics are made exclusively from synthetic raw materials. The term non-oxide ceramics generally refers to carbides, nitrides, borides or oxynitrides.

Covalent Bonds → Remarkable Properties

Silicon carbide (SiC) is the most widely used nonoxide ceramic. It is synthesized by Acheson process which involves mixing high-quality silica sand (99.5% SiO2) with coke (carbon) in a large elongated mound and placing carbon electrodes in opposite ends. The core contains green hexagonal α phase SiC, formed at >2000°C with low level of impurities. The rest contains the cubic β phase, which is formed in the range 1400–1800°C, with lower purity. At around 2200 °C the coke reacts with the SiO2 to produce SiC plus CO:

$$SiO_2\ (s) + 3C\ (s) \rightarrow SiC\ (s) + 2CO\ (g)$$

SiC is not stable at high temp in an oxygen environment. Good thermal shock (High thermal conductivity), good strength (512 MPa) and high hardness. Density $\rho = 3.21 g/cm^3$

Silicon Nitride

Silicon nitride (Si_3N_4) is another synthetic mineral. It occurs in two crystalline forms. The lower temperature α form is usually preferred as a raw material because the transformation to the β form during sintering favors the development of an elongated crystal structure.

1) Nitridation of Si powder at 1250-1400^{o}C  $3Si\ (s) + 2N_2\ (g) \rightarrow Si_3N_4\ (s)$

Other routes: 2) Carbothermal reduction of silica in N_2 in the range 1200–1550^{o}C:

$3SiO_2\ (s) + 6C\ (s) + 2N_2\ (g) \rightarrow Si_3N_4\ (s) + 6CO\ (g)$

3) Vapor phase reaction of $SiCl_4$ or silane (SiH_4) with ammonia

Titanium Carbide

Titanium carbide (TiC) is another nonoxide ceramic that is not available in nature. It is prepared either by the carbothermal reduction of TiO_2 or by direct reaction between the elements titanium and carbon. As in many of these reactions high temperatures are required. The carburization temperature is between 2100 and 2300^{o}C.

Boron Carbide B_4C

It is the third hardest materials known, behind cubic Boron Nitride (BN) and Diamond. It is used in tank armor, bulletproof vests, and numerous industrial applications.

Boron Nitride BN

The hexagonal form corresponding to graphite is the most stable and softest among BN polymorphs, and is therefore used as a lubricant and an additive to cosmetic products. The hardness of the conventional form is called c-BN inferior only to diamond.