9 Ceramic biomaterials

9.1 How one can define "ceramics"? Discuss the properties of ceramics based on their bonding types. Classify the applications and give examples for the ceramic biomaterials.

Ceramic materials, group of solid states, include ceramics, glasses, and glass-ceramics, consisting of inorganic, nonmetallic compounds.

The term "ceramics" covers inorganic, non-metallic materials whose formation is due to the action of heat.

The American Society for Testing and Materials (ASTM) defines a ceramic article as "an article having a glazed or unglazed body of crystalline or partly crystalline structure, or of glass, which body is produced from essentially inorganic, nonmetallic substances and either is formed from a molten mass which solidifies on cooling, or is formed and simultaneously or subsequently matured by the action of the heat."

Ceramics are known to be hard, brittle, and often porous, explained by the nature of bonds between the atoms.

Chemical composition of ceramics:

- Ceramic materials are inorganic (In general they do not have covalent bonds. But some ceramics could have covalent bonds, for example, diamond or graphite), nonmetallic (In general, no metal bonds are present, but some ceramics (advanced ceramics) could have metal bounds) (ionic-bonded) solids, usually metal oxides.
- Some kinds of ceramics (advanced ceramics) are compounds of metals and carbon, nitrogen, or sulfur. Advanced ceramics have to some extend metallic bonds.
- Diamond and graphite are sometimes considered to be ceramics even though they are not composed of inorganic compounds.
- Chemical bonds occurring in ceramics are covalent, ionic, metallic or polar covalent bonds depending on the chemical composition of the ceramics.

General properties of ceramics

- The crystalline or amorphous ceramics are ionic or covalently bonded. Therefore, they are usually less dense than metals and tend to fracture before plastically deformed. There exist special routes of deformation. Thus, the toughness is poor and becomes even worse as the result of defects including pores.
- Ceramics are hard but brittle and can withstand high temperatures.
- Several ceramics are semiconducting and are, therefore, used as (bio-)sensors.
- Although ceramics are also superconducting, often they are perfect insulators, because free charges are absent.
- Ceramics are in general more corrosion resistant than other materials.

Classification of bioceramics
Ceramic implant materials are:

- inert (bioinert), i.e. remain unchanged:
  - Oxide ceramics (titania (TiO_2), alumina (Al_2O_3), zirconia (ZrO_2));
  - Silica ceramics (silica glasses);
  - Pyrolytic (glass-like) carbons.
- absorbable, i.e. they dissolve within a certain period of time;
- active (bioactive), i.e. incorporated into (different) physiological processes
  - Calcium phosphates (very different ones, including hydroxyapatite);
  - Bioactive glass (glass-ceramics).

Ceramics are used in the form of:

- highly polished parts of artificial joints (hardness and wear resistance);
- (parts of) degradable or non-degradable bone cements;
- part(s) of composite materials including dental applications;

- coatings of metals;
- micro-spheres or porous networks, for example as bone spacer to replace larger pieces of bone removed because of disease or trauma.

9.2 Discuss a typical fabrication process of ceramic biomaterials and compare it with biomineralization.

Ceramics are *technically* produced by **mixing the constituents and heat treatment**. (This is called combustion. **Combustion** or burning is the sequence of exothermic chemical reactions between a fuel and an oxidant accompanied by the production of heat and conversion of chemical species.)

Biomineralization is based on the organic-inorganic interplay concerted by an organism. (Biomineralization is the process by which living organisms produce minerals.)

Biomineralization: basic principles
Nucleation takes place at specific centers in organic matrix.
In most cases, the (strongly) acidic proteins bind the cations. The anions bind together and form the mineral (mineralization).
The defined crystal size and geometry results from the specific adsorption of proteins at crystal surfaces of defined orientation. Nature tailors the crystal growth.
Mineralization is the interplay of promotors and inhibitors, whereby a kinetic process with thermodynamic restrictions.
Within the human body we observe bone formation and the growth of teeth (enamel and dentin).

General processes to fabricate ceramics

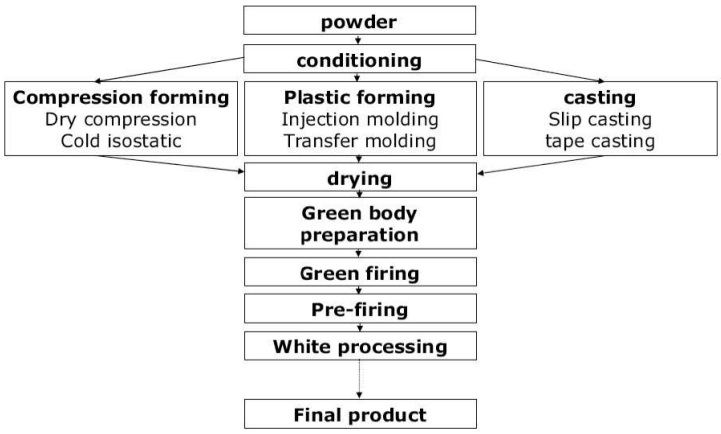

Figure 1: General processes to fabricate ceramics.

Typical fabrication process of ceramic biomaterials
The traditional ceramic process generally follows this sequence: Milling → Batching → Mixing → Forming → Drying → Firing → Assembly

- Milling is the process by which materials are reduced from a large size to a smaller one.
- Batching is the process of weighing the oxides according to recipes, and preparing them for mixing and drying.
- Drying is removing the water or binder from the formed material. Spray drying is widely used to prepare powder for pressing operations.

Manufacture of advanced ceramics
The preparation of an advanced ceramic material usually begins with a finely divided powder that is mixed with an organic binder to help the powder consolidate, so that it can be molded into the desired shape. Before it is fired, the ceramic body is called "green." The green body is first heated at a low temperature in order to decompose or oxidize the binder. It is then heated to a high temperature until it is "sintered," or hardened, into a denser, strong ceramic. At this time, individual particles of the original powder fuse together as chemical bonds form between them. During sintering the ceramic may shrink by as much as 10 to 40 percent. Because shrinkage is not uniform, additional machining of the ceramic may be required in order to obtain a precise shape.

Sol-gel technology
Sol-gel technology allows better mixing of the ceramic components at the molecular level, and hence yields more homogeneous ceramics, because the ions are mixed while in solution. In the sol-gel process, a solution of an organometallic compound is hydrolyzed to produce a "sol," a colloidal suspension of a solid in a liquid. Typically the solution is a metal alkoxide such as tetramethoxysilane in an alcohol solvent. The sol forms when the individual formula units polymerize (link together to form chains and networks). The sol can then be spread into a thin film, precipitated into tiny uniform spheres called microspheres, or further processed to form a gel inside a mold that will yield a final ceramic object in the desired shape. The many crosslinks between the formula units result in a ceramic that is less brittle than typical ceramics.
Although the sol-gel process is very expensive, it has many advantages, including low temperature requirements; the ceramist's ability to control porosity and to form films, spheres, and other structures that are difficult to form in molds; and the attainment of specialized ceramic compositions and high product purity.
Porous ceramics are made by the sol-gel process.

9.3 What are typical calcium phosphate phases (CPP)? Why it is possible to classify them in acidic, neutral and alkaline? Which methods you know to discriminate the different phases?

Calcium phosphate is the name given to a family of minerals containing calcium ions (Ca^{2+}) together with orthophosphates (PO_4^{3-}), metaphosphates or pyrophosphates ($P_2O_7^{4-}$) and occasionally hydrogen or hydroxide ions.

Varieties of Calcium Phosphate:

- Tricalcium phosphate - $Ca_3(PO_4)_2$ (also called tribasic calcium phosphate; occurs in alpha and beta phases, beta also known as Whitlockite)
- Dicalcium phosphate - $CaH(PO_4)$ (also called calcium monohydrogen phosphate)
- Calcium dihydrogen phosphate - $Ca(H_2PO_4)_2$ (also called monocalcium phosphate)

- Calcium pyrophosphate - $Ca_2P_2O_7$ (occurs as alpha, beta and gamma phases)
- Hydroxylapatite - $Ca_{10}(PO_4)_6(OH)_2$

Ca : P	Mineral name	Formula	Chemical name
1.0	Monetite	$CaHPO_4$	Dicalcium phosphate (DCP)
1.0	Brushite	$CaHPO_4 \cdot 2H_2O$	Dicalcium phosphate Dihydrate (DCPD)
1.33	—	$Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$	Octocalcium phosphate (OCP)
1.43	Whitlockite	$Ca_{10}(HPO_4)(PO_4)_6$	
1.5	—	$Ca_3(PO_4)_2$	Tricalcium phosphate (TCP)
1.67	Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	
2.0		$Ca_4P_2O_9$	Tetracalcium phosphate

Figure 2: Calcium phosphate phases with respect to structure and Ca/P ratio.

Methods to discriminate the different phases:

- **Debye-Scherrer method**
  Debye-Scherrer Method - a method for studying the structure of finely crystalline substances using X-ray diffraction (powdered-crystal method). Powder diffraction is a scientific technique using X-ray, neutron, or electron diffraction on powder or microcrystalline samples for structural characterization of materials. The most widespread use of powder diffraction is in the identification and characterisation of crystalline solids, each of which produces a distinctive diffraction pattern. Both the positions (corresponding to lattice spacings) and the relative intensity of the lines are indicative of a particular phase and material, providing a "fingerprint" for comparison (see Fig.4). A multi-phase mixture, "e.g." a soil sample, will show more than one pattern superposed, allowing for determination of relative concentration.

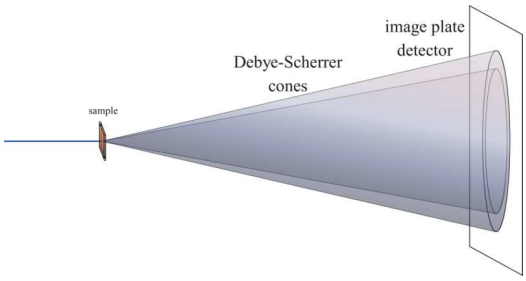

Figure 3: Debye-Scherrer Method

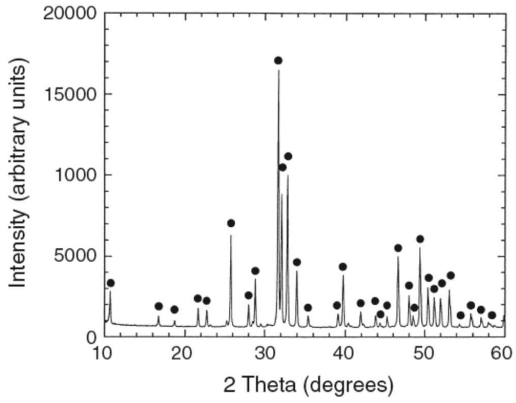

Figure 4: X-ray diffraction of hydroxyapatite.

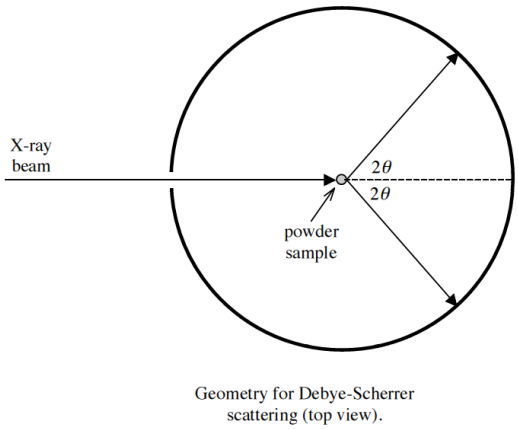

Figure 5: Geometry for Debye-Scherrer scattering (top view).

Phases of calcium phosphates have characteristic pH values. As a result it is possible to classify them in acidic, neutral and alkaline.
The dissolution of β -tricalcium phosphate (TCP) lowers the pH, whereby the dissolution of tetracalcium phosphate results in an pH increase.

9.4 Please describe the electrochemical-assisted deposition (ECAD) of calcium phosphate phases (on titanium implants) and discuss the advantages of the method.

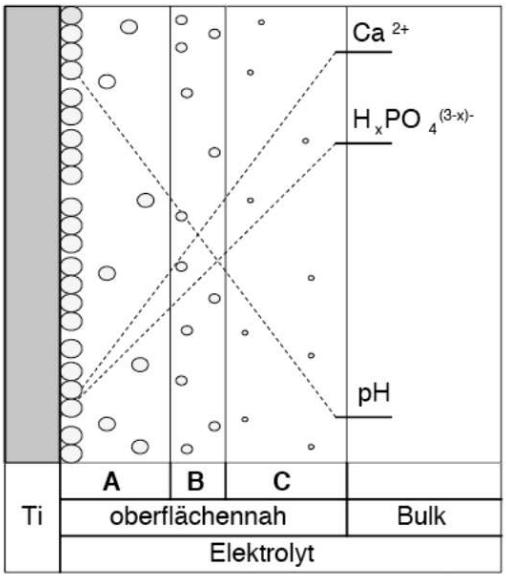

Figure 6: Scheme of electrochemicalassisted deposition (ECAD) of calcium phosphate phases (CPP).A: nuclei growth and adsorption; B: nuclei formation; C: sub-critical nuclei.

Chemical precursors are sprayed across electrostatic field towards a heated substrate, the chemical undergo a controlled chemical reaction and are deposited on the substrate.
Using sufficient supersaturated solutions is impractical for production lines. Alternatively, one can realize supersaturation near substrate's surface by cathode polarization. The electro-chemical processes include:

$$H_2O + 2e^- \rightarrow H_2 + 2OH$$
$$O_2 + 4e^- + 2H_2O \rightarrow 4OH$$

Advantages of ECAD:

- ECAD is low temperature process, that will not affect the structure of the implant;
- can be used for determining the composition of the sample. For example, how pure the material is.
- it does not require any vacuum or electron beam, so it reduces the costs, material and power;
- it uses electrostatic field to coat complex 3D parts.

9.5 Discuss the advantages of bioglasses with respect to thermally treated calcium phosphate phases.

Bioglasses are amorphous solid states, in general case. That is why they are less stable than solid state materials, and their solubility is higher.

The advantages of thermally treated calcium phosphate phases as implant materials is related to the fact that they are especially biologically inactive. In comparison, bioglasses are biologically active and form an interfacial bond with tissues.

The rate of bonding of bioactive glasses depends on many factors. One is bulk composition: the most rapid rates of bonding for bioactive glasses composed of SiO_2, CaO, Na_2O and P_2O_5 are obtained with SiO_2 contents of 45-52% weight. In this compositional range, a bonding both to soft and hard connective tissue occurs within 5-10 days. Bioactive glasses or glass-ceramics containing 55-60% SiO_2 require a longer time to form a bond with bones, and do not bond to soft tissues. Glass compositions with more than 60% SiO_2 do not bond either to bone or to soft tissues, and elicit formation of a non adherent fibrous interfacial capsule.

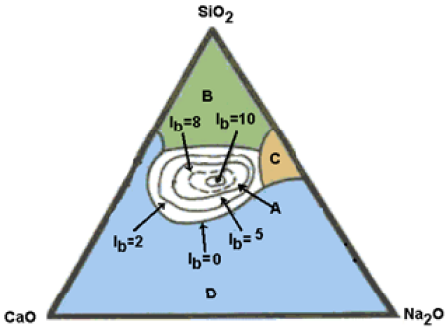

Figure 7: Bioactive regions of bioglasses.

Glasses and glass-ceramics that have a composition falling inside region A develop HA both in-vitro and in-vivo. Compositions inside the dashed line bind also to soft tissues. The materials in region B are inert, and those in region C are resorbable. Region D is a non-glass forming and nonbonding region.
I_b- index of bioactivity, a measure of the level of bioactivity of bioactive materials, and is defined as the inverse of the time required for more than 50% of the interface to be bonded.