Ceramics, Glasses, and Glass-Ceramics

- Ceramics, Glasses, and Glass-Ceramics include a broad range of inorganic/nonmetallic compositions.
  - Eyeglasses
  - Diagnostic instruments
  - Thermometers
  - Tissue culture flasks
  - Fiber optic for endoscopy
  - Dentistry (gold-porcelain crowns, glass-filled ionomer cements, and dentures)

Ceramics, Glasses, and Glass-Ceramics

- Refractory compounds/materials
- Usually some combination of metal and nonmetal in general

$\mathbf{A_mX_n}$ structural form (A = metal; X = nonmetal)

- Relative size of ions (radius ratio) and degree of covalent/ionic bonding determine atomic arrangements.
- High oxidized state and ion/covalent bonding in ceramics makes them:
  - Resistant to oxidation and increases stability
  - Nonconducting
  - High melting temps
  - Hard and brittle

Ceramics, Glasses, and Glass-Ceramics

- Generally used to repair or replace skeletal hard connective tissue.

- No one material is suitable for all biomaterial applications.

  - Their success depend upon achieving a stable attachment to connective tissue.
  - Tissue attachment is directly related to the type of tissue response at the implant-tissue interface.
  - No material implanted is inert; all materials elicite a response from the tissue.

Ceramics, Glasses, and Glass-Ceramics

- 4 types of tissue response:

TABLE 1 Types of Implant–Tissue Response

If the material is toxic, the surrounding tissue dies.
If the material is nontoxic and biologically inactive (nearly inert), a fibrous tissue of variable thickness forms.
If the material is nontoxic and biologically active (bioactive), an interfacial bond forms.
If the material is nontoxic and dissolves, the surrounding tissue replaces it.

Ceramics, Glasses, and Glass-Ceramics

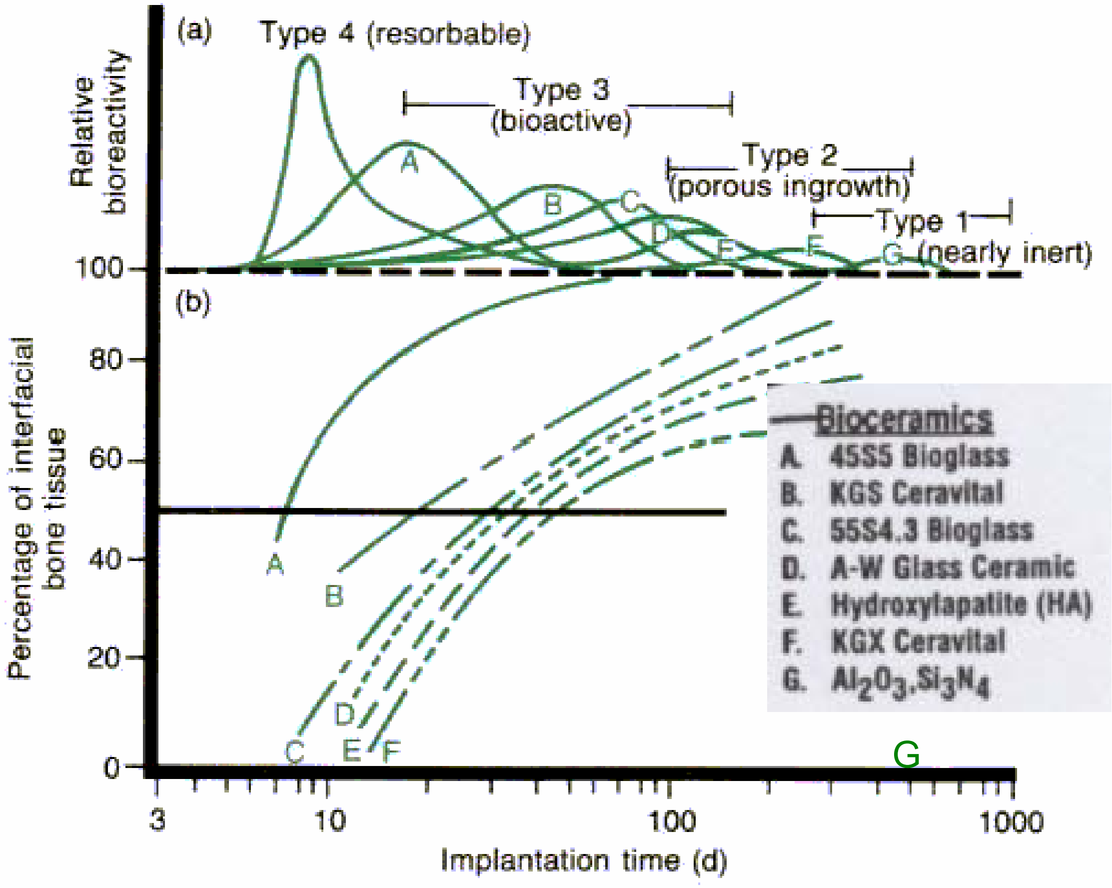
- 4 different means of attaching prostheses to the skeletal system:

TABLE 2 Types of Bioceramic–Tissue Attachment and Their Classification

Type of attachment	Example
1. Dense, nonporous, nearly inert ceramics attach by bone growth into surface irregularities by cementing the device into the tissues or by press-fitting into a defect (termed "morphological fixation").	Al_2O_3 (single crystal and polycrystalline)
2. For porous inert implants, bone ingrowth occurs that mechanically attaches the bone to the material (termed "biological fixation").	Al_2O_3 (polycrystalline) Hydroxyapatite-coated porous metals
3. Dense, nonporous surface-reactive ceramics, glasses, and glass-ceramics attach directly by chemical bonding with the bone (termed "bioactive fixation").	Bioactive glasses Bioactive glass-ceramics Hydroxyapatite
4. Dense, nonporous (or porous) resorbable ceramics are designed to be slowly replaced by bone.	Calcium sulfate (plaster of paris) Tricalcium phosphate Calcium-phosphate salts

Ceramics, Glasses, and Glass-Ceramics

- The relative reactivity correlates closely with the rate of formation of an interfacial bond of implants with bone.



Ceramics, Glasses, and Glass-Ceramics

- The relative level of reactivity of an implant influences the thickness of the interfacial zone or layer between the material and tissue.

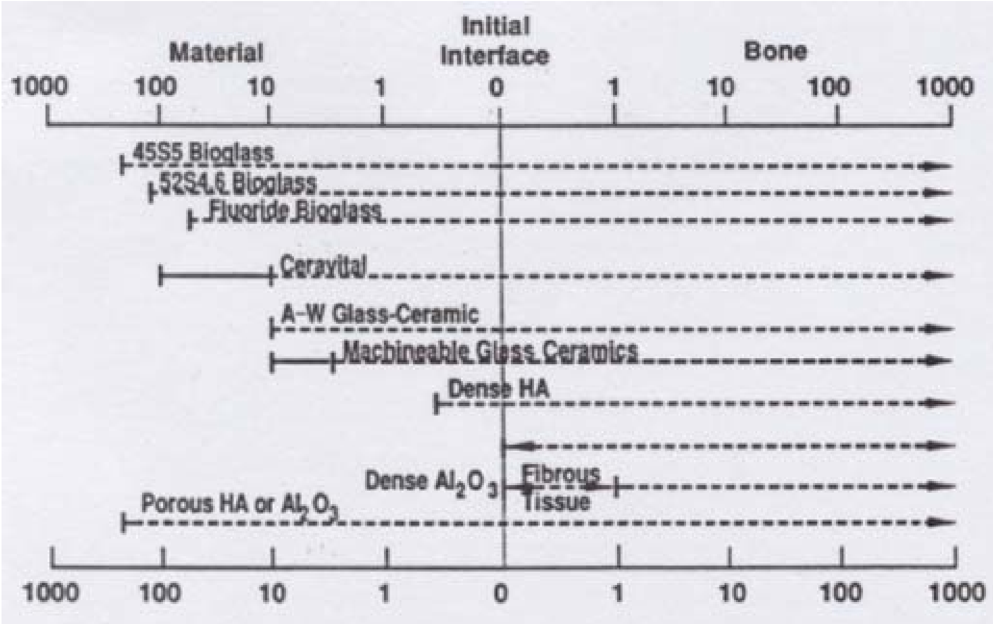


FIG. 2. Comparison of interfacial thickness (μm) of reaction layer of bioactive implants of fibrous tissue of inactive bioceramics in bone.

Bioceramics

- Ceramics are:
  - Stiff
  - Hard
  - Chemically stable
  - Wear resistant
- Material properties differ greatly dependent on (thermal) processing method, yielding 5 categories of microstructure:
  - Glass
  - Cast or plasma-sprayed polycrystalline ceramic
  - Liquid-sintered (vitrified) ceramic
  - Solid-state sintered ceramic
  - Polycrystalline glass-ceramic
- Of the large number of ceramics known only a few are suitable biocompatible. Main problems:
  - They are brittle
  - Relatively difficult to process

Bioinert Bioceramics

(nearly inert crystalline ceramics)

- Elicit minimal response from host tissue
- Forein body response = encapsulation
- Undergo little physical/chemical alteration in vivo
- Types:
  - **Alumina (Al_2O_3 >99.5% pure)**
  - Partially stabilised zirconia (ZrO_2)
  - Silicon nitride (Si_3N_4)
- Functional properties
  - High compressive strenght
  - Excellent wear resistance
  - Excellent bioinertness

Bioinert Bioceramics: Alumina (Al_2O_3)

- High density , high purity (>99.5%) alumina
- Used for >30 years
- Very chemically inert
- Excellent corrosion resistance
- High wear resistance, but
- Low fracture thoughness and tensile strenght (high elastic moculus)
- Used in compression only (to reduce encapsulation thickness)
  - Femoral head of total hip replacements
  - Orthopedic implants in generel
  - Dental implants

Dental Ceramics

- Excellent aesthetics (opaqueness & color)
- Very tough and hard material
- But brittle; improvements of strenght necessary (achieved by proper processing)
- Expensive manufacture (dental labs)
- Alteration of opaqueness & color possible

Porous Ceramics

- Advantage:
  - Inertness
  - Mechanical stability of implant (bone ingrowth at poresize>100µm)
- Disadvantage
  - Restricition to non-load bearing applications
  - Weaker, larger surface exposed
- Microstructure of certain corals (hydroxyapatite) is almost ideal:
  - Machine the coral to desired shape.
  - Fire off CO_2 (from $CaCO_3 \rightarrow CaO$) while microstructure is maintained.
  - Casting desired material into the pores (Al_2O_3, TiO_2,..).
  - Removing of CaO by HCL.

FIG 2: A scanning electron micrograph of porous (spongy) bone.

Bioactive Glasses and Glass- Ceramics

- Common characteristics:
  - time-dependent modification of the surface → formation of a biologically active carbonated HA layer (hydroxy apatite) that provides the bonding interface with tissue.

- Direct chemical bond with tissue (in particular bone)
- Low mechanical strength and fracture thoughness

- Applications:
  - Coatings on stainless steel, Ti, and CoCr for tissue ongrowth
  - Bone filler for dental and maxillofacial reconstruction

Bioactive Glass and Glass-Ceramis

Bioactive Glass: Compared to traditional soda-lime-silica glasses: less SiO_2, high Na_2O and CaO, and high CaO/P_2O_5 ratio => surface highly reactive in aqueous medium

Ceramic	Al_2O_3 (wt%)	ZrO_2 (wt%)	SiO_2 (wt%)	Na_2O (wt%)	CaO (wt%)	P_2O_5 (wt%)	MgO (wt%)	CaF_2 (wt%)
Bioglass® (45S5 Glass)			45.0	24.5	24.5	6.0		
Ceravital (Glass-Ceramic)			40-50	5-10	30-35	10-50	2.5-5.0	
Cerabone (AW) (Glass Ceramic)			34.0		44.7	16.2	4.6	0.5
High Alumina (Ceramic)	>99.0							
Partially Stailized Ziconia		>97.0						
Sintered HA								

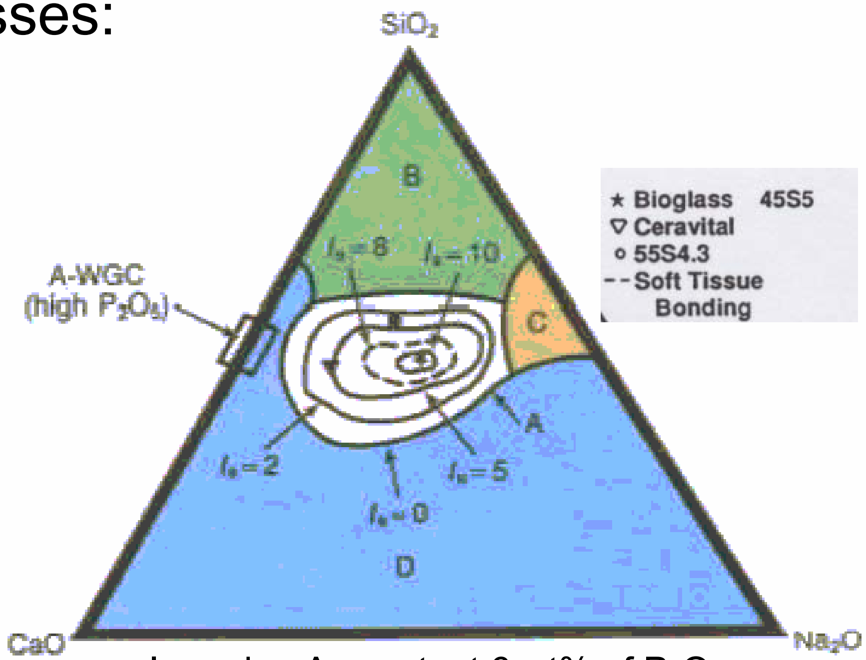
Inclusion of even small amounts of metal oxides strongly reduces bioactivity

Courtesy R. Zenz

Bioactive Glass

- Compositional dependence of bone and soft tissue bonding on the Na_2O-CaO-P_2O_5-SiO_2 glasses:

  - A: bioactive, bone bonding
  - B: nearly inert; formation of a fibrous capsule
  - C: resorbable (within 10-30 days)
  - D: not technically practicable



In region A constant 6 wt% of P_2O_5.

  - I_B-value (index of bioactivity): is 100/ (time take to achieve 50% of interface to be bonded)

Bioactive Glass

Bioceramic	I_b value
45S5 Bioglass	12.5
Ceravital	5.6
A/W Glass-Ceramic	3.2
HA	3.1
Al_2O_3	0

- Addition of multivalent cations shrinks the iso I_B-contour.
  - Al_2O_3, Ta_2O_5, TiO_2, Sb_2O_3, or ZrO_2
  - E.g. 3% Al_2O_3 to 45S5 prevents bone binding.

Bioactive Glass

- Implants near the I_B boundary ($I_B = 0$) require more precise surgical fit and longer fixation times.
- Intermediate I_B:
  - Do not develop stable soft tissue bonds.
  - The fibrous interface progressively mineralizes to form bone.
    - A-W glass ceramic ($I_B = 3{,}2$)
      - 10-20µm interfacial thickness
      - High resitance to shear
- $I_B > 8$: formation of stable bone and soft tissue bonding depending on the progenitor stem cell in contact with the implant.
    - 45S5 Bioglass ($I_B = 12{,}5$)
      - 200µm interfacial thickness
      - Relatively low shear resistance

Calcium phosphate Ceramics

- Calcium phosphate based bioceramics used in medicine and dentistry for more than 20 years.
- At body temperature only 2 calcium phosphates are stable when in contact with aqueous media such as body fluid:
  - pH<4,2 — $CaHPO_4 \cdot 2H_2O$ (dicalcium phosphate)
  - pH≥4,2 — $Ca_{10}(PO_4)_6(OH)_2$ (HA, hydroxyapatite) (60-70% of the mineral phase of the human bone)

Table 1. Intermediate compounds in the formation of HAp[18,19]

Name	Abbreviation	Chemical Formula	Ca/P
Hydroxyapatite	HAp	$Ca_{10}(PO_4)_6OH_2$	1.67
Carbonated hydroxyapatite	CHA	$Ca_{10}(PO_4)_6CO_3$	1.67
Fluorapatite	FHA	$Ca_{10}(PO_4)_6F_2$	1.67
α, β - tricalcium phosphate	α, β - TCP	α, β - $Ca_3(PO_4)_2$	1.55
Amorphous calcium phosphate	ACP	$Ca_9(PO_4)_6$	1.55
Octacalcium phosphate	OCP	$Ca_8H_2(PO_4)_6$	1.33

Calcium phosphate Ceramics

- Resorbable or bioactive
- Applications:
  - Coatings for chemical bonding to bone (orthopedic, dental and maxillofacial prosthetics)
  - Dental implants
  - Temporary bone space fillers
- Mechanical behavior (tensile and comprehensive strenght, fatique resistance) depend on the total volume of porosity, generally inferior.
- Resorbable calcium phosphates
  - Physiochemical dissolution (depends on the local pH-value)
  - Physical disintegration into small particles (result of preferential chemical attack of grain boundaries).
  - Biological factors (e.g. Phagocytosis)

Calcium phosphate Ceramics

- Increasing degradation rate: α-TCP>β-TCP>>HA
- Increasing rate of biodegradation:
  - Increased surface area (porous solid>dense solid)
  - Decreased crystallinity
  - Decreased crystal and grain size
  - Presence of ionic substitutes (CO_3^{2-}, Mg^{2+}, Sr^{2+}) in HA
- Decreased rate of biodegradation:
  - F^- substitution in HA
  - Mg^{2+} substitution in β-TCP
  - Lower β-TCP/HA ratio in biphasic phosphates

Resorbable Ceramics

- Chemically brocken down by the body and resorbed (ability to be processed through normal metabolic pathways)
- Dissolution rate is controlled by composition and surface area. (ideally a composition should be used that is slowly resorbed by the body once new bone formation is complete)
- Calcium phosphate ceramics
  - e.g., tri-calcium phosphate (TCP): $Ca_3(PO_4)_2$

  (lower Ca/PO4 ratio than HA)
- Application:
  - Bone repair (maxillofacial and peridontal defects)
  - Temporary scaffold or space-filler, bone-cement which is gradually replaced by tissue.