

CERAMICS: Structure 2 (Compositions and Defects)

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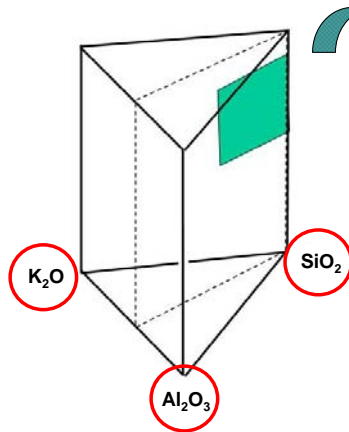
Nex, let's consider key concepts about ceramic compositions and defects.

COMPOSITION

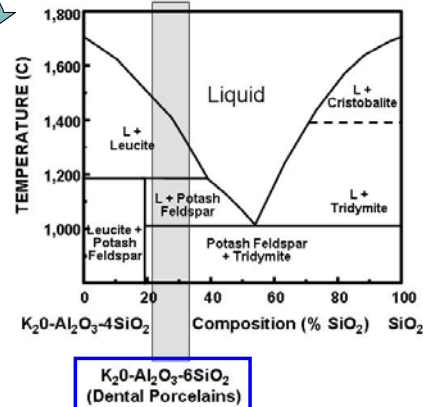
Porcelain phase diagram.

- Review: Dental porcelain = $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$
- Created by mixing clay, feldspar, and quartz having mixed components

TERNARY PHASE DIAGRAM
for $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$



PSEUDO-BINARY PHASE DIAGRAM
for $4\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$ with SiO_2



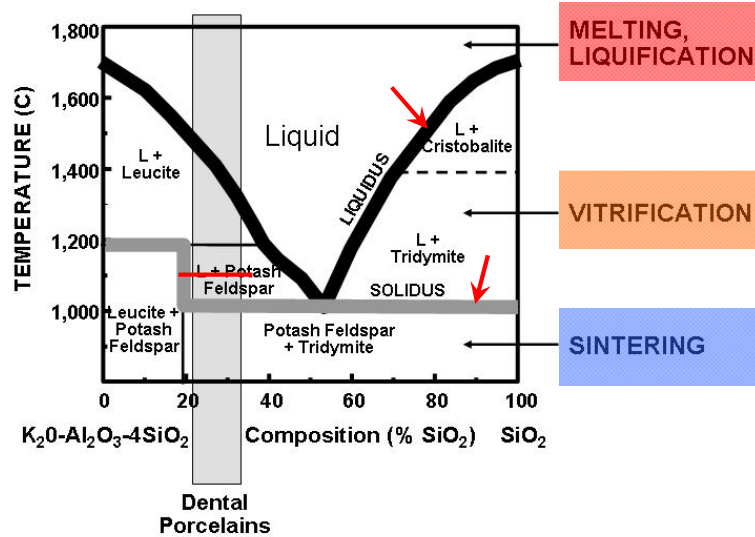
Dental porcelain is an extremely important composition for dentistry. Remember that porcelain is a combination SiO_2 (silica), Al_2O_3 (alumina), and K_2O (potassium oxide). Instead of mixing the pure oxides, porcelain is generally created by combining clay (hydrated alumino-silicate), feldspar (alumino-silicate), and quartz (silica) which includes some potassium oxide in the first two.

To be able to follow the important phase transitions that occur, we would like to examine the phase diagram. **[CLICK]** The main components form a ternary diagram (seen on the left) that is a 3D solid with the components at the corners. **[CLICK]** The potassium oxide and alumina components are generally about equal in molar ratios with only the silica changing in the compositions of interest. Therefore, we can create a slice through the diagram for the compositions and temperatures of interest and **[CLICK]** extract it as a PSEUDO-BINARY phase diagram. That is shown on the right. **[CLICK]** Dental porcelains represent a narrow range that are close to $6\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$.

Next it is important to examine the features of the pseudo-binary slice so that we understand the fabrication technologies for porcelains.

COMPOSITION

Pseudo-binary phase diagram for porcelain.



All the same types of features are present but slightly distorted by the fact that we are looking at a slice rather than a true phase diagram. Examine the figure and its labels. **[CLICK]** The LIQUIDUS line is bolded black. **[CLICK]** The SOLIDUS line is bolded gray.

[CLICK] Above the liquidus is melting or liquefaction.

[CLICK] Between the liquidus and solidus there are L+S phases. We are often dealing with a compacted powder as a solid. If we heat it into this range, parts of the powder melt and the pieces consolidate and flow together to form a continuous solid. This is a traditional fabrication procedure for commercial ceramic objects like pots, plates, sinks, or artistic objects.

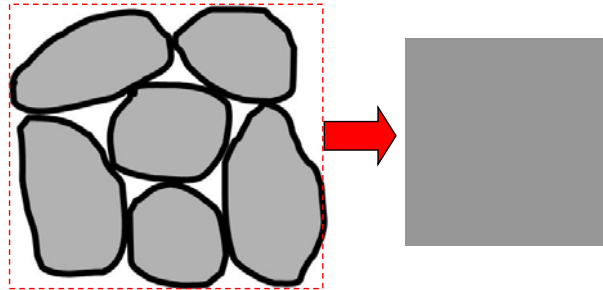
[CLICK] If you cannot or choose not to heat a compacted powder solid above the solidus line, you can still get consolidation. Diffusion occurs at powder contacts and material slowly rearranges itself to form a solid. This is called SINTERING. It can be accomplished with heat alone but is faster with heat and pressure, particularly at lower temperatures. As we will encounter later, some dental materials are created by hot isostatic pressing (H.I.P.) which uses heat and pressure at moderate temperatures.

See if you can use the diagram. If you chose a dental porcelain composition, use compacted powder to form the intended shape, and heat the compact to 1100 C **[CLICK]**, what type of solidification (consolidation) process would occur? This is in a L+S region. This is VITRIFICATION. What phases would exist? There are 2 phases. There is a liquid phase and a solid phase called potash feldspar. You could figure out the specific compositions and amounts with tie lines and the lever law. You are not expected to be able to do that.

Next let's look more closely at vitrification and sintering.

VITRIFICATION

Consolidation (or densification) of compacted powders of ceramic.



65% packing efficiency;
35% porosity

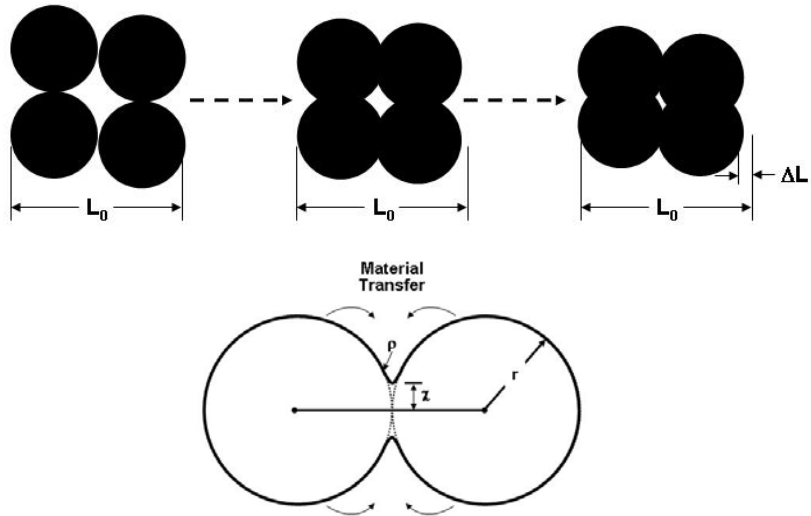


Ceramics have high melting temperatures. Generally they are manipulated as powders which are packed into the intended shapes and then heated. To facilitate the process, sometimes the powders are slurried with water and painted into place onto molds. The powder sticks together because of weak electrostatic forces among the particles.

[CLICK] Once this powder compact is heated into the L+S region, **[CLICK]** as L forms, the remaining material flows together and spaces between the particles are eliminated. **[CLICK]** The powder is generally packed to fill about 65% of space. **[CLICK]** Therefore, it shrinks 35%. This must be planned in the creation of any object whose dimensions are critical. In dentistry, we generally build porcelain in layers to accommodate for the shrinkage and have color control of the final object.

SINTERING

Consolidation of powder with heat and/or pressure.

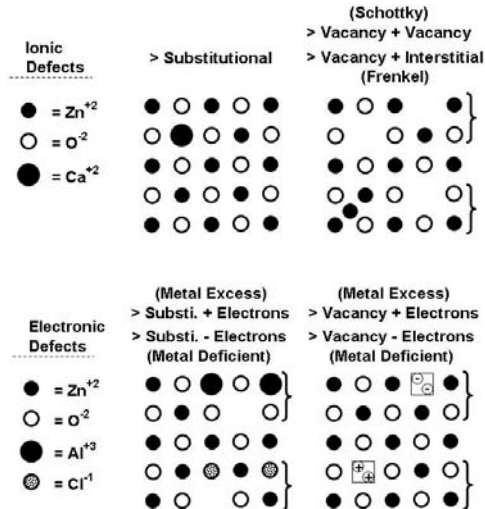


If there is no liquid present to facilitate consolidation, then SOLID STATE DIFFUSION is required. The process looks a lot the same from a local perspective. There is still about 35% shrinkage. In the figure, only the length (L_0) is indicated for part of the process.

If you examine the contact area between two adjacent particles **[CLICK]** you will see exactly what is going on. Material is being transferred from the particles to the high energy contact zones and filling in the spaces between the particles. This makes the centers move closer and closer together until the particle boundaries disappear. If the process stops or slows down near the end, then there will be small pores remaining in the microstructure. Clearly this is not advantageous.

DEFECTS

Types of point defects in ceramics.



Ceramics have the same type of defects as metals (vacancy, substitutional, interstitial) but they are more complicated by the fact that often the ceramics are ionically bonded and must maintain an overall charge balance. **[CLICK]** You cannot have a net positive or negative charge on the solid at equilibrium.

[CLICK] If you substitute or remove a positive or negative ion (substitutionals and vacancies), you must balance it out with a counter-veiling one. You can see how this works in the figure for vacancies to create Schottky or Frenkel defects. You do NOT need to know these terms. Simply be aware that CHARGE BALANCE is important in the process.

[CLICK] In this case, we looked at similarly charged ions. However, you can you employ ions with different charges and this creates another problem for charge balancing in the solid. The image is simply presented to show you that the process is possible.

DEFECTS

Types of line, area, and volume defects in ceramics.

Point defects (previously described)

Vacancy
Substitutional
Interstitial

Line Defects

Dislocations

Area Defects

Stacking faults
Grain boundaries

Volume Defects

Pores, Voids,
Cracks



Defects associated
with crystalline
phases only.



Other defects in ceramics are the same as for metal systems that we have already described.

[CLICK] Line defects like dislocations are complicated by the fact neighboring ions typically alternate in charge – and so dislocation movement is much more difficult. It requires movements of two ionic positions. **[CLICK]** Area defects exist. **[CLICK]** Volume defects exist.

[CLICK] The major difference is that ceramics often are partly or totally non-crystalline. Many of these defects are only associated with the crystalline phase. The fact that these defects are more difficult to move around and only associated with crystalline phases, means that the most important types of defects for most dental materials are usually pores and cracks. **[CLICK]** In the next modules we will focus on them. They are primarily responsible for the properties of interest.

QUICK REVIEW

Review of (A-B)-C-D for ceramics structure.

- **What are the 3 major COMPONENT OXIDES of porcelain?**
SiO₂, Al₂O₃, K₂O
- **What is a VERTICAL SLICE through a ternary phase diagram called?**
PSUEDO-BINARY PHASE DIAGRAM
- **What is a typical MOLAR RATIO of dental porcelain components?**
~6SiO₂:1Al₂O₃: 1K₂O
- **What is the NAME for powder consolidation with L+S phases?**
VITRIFICATION
- **What is the NAME for powder consolidation with only S phases?**
SINTERING
- **What REQUIREMENT complicates formation of ionic defects?**
CHARGE BALANCE
- **What CATEGORY of defects is most important for dental ceramics?**
VOLUME DEFECTS (PORES AND CRACKS)



Here is a quick review of the concepts from this module.

[CLICK] (1) What are the 3 major COMPONENT OXIDES of porcelain?

[CLICK]

[CLICK] (2) What is a VERTICAL SLICE through a ternary phase diagram called?

[CLICK]

[CLICK] (3) What a the typical MOLAR RATIO of dental porcelain components?

[CLICK]

[CLICK] (4) What is the NAME for powder consolidation with L+S phases?

[CLICK]

[CLICK] (5) What is the NAME for powder consolidation with only S phases?

[CLICK]

[CLICK] (6) What REQUIREMENT complicates formation of ionic defects?

[CLICK]

[CLICK] (7) What CATEGORY of defects is most important for dental ceramics?

[CLICK]



THANK YOU



THANK YOU.