Lecture 8

Effects of Processing on Properties

Introduction:

Crafting a ceramic is similar to building a pyramid. It starts with a base, which, in this case, is the starting grain or powders. Everything depends on the base, and when it is insecure, the pyramid will not stand.

Both microstructure and superior properties derive from the starting materials, provided that these materials are handled with respect throughout the remaining processing. Preceding chapters addressed how careful handling is accomplished. Remaining to be addressed is the important task of understanding the results.

This chapter describes how materials selection and processing affects the properties of the final ceramic.

Selection of Materials:

The characteristics of the starting materials are crucial and complex: there are many alternatives that depend on what is to be accomplished. Addressed below are three important factors: physical properties of the phases, chemical properties of the phases, and the final microstructure of results from the materials selected at the beginning. These preceding factors serve as guiding restraints; the final selection comes from experience.

Physical Properties of the Phases:

Different materials have unique intrinsic properties that derive from the chemical bonding and crystal structure of the lattice. The initial choice of powdered and granular materials depends upon these properties.

Melting Point

The melting point of the phase limits the material’s temperature applications.

Thermal Conductivity

High conductivity reduces thermal shock and conducts heat.

Materials with low thermal conductivity are useful thermal insulators.

Thermal Expansion

High expansion increases the tendency for thermal shock to occur.

Heat Capacity

High heat capacity retards heating and cooling.

Electronic Conductivity

Different applications require either conductors or insulators.

Ionic Conductors

Such conductors are used in oxygen sensors and fuel cells.

Hardness

As a general rule, hard materials are more wear resistant. However, exceptions to this rule do exist.

Chemical Properties of the Phases

Chemical properties determine which phase will be stable at a particular temperature as well as the reactivity of a given application.

Thermodynamics

The free energy of formation predicts reactions occurring at elevated temperatures. Thermodynamics also predicts the phases that are stable at different temperatures. Many phase diagrams exist and are useful aids when selecting the starting raw materials.

Solubility

A material can dissolve when it contacts a liquid. Because most phase diagrams do not provide solubility information; a material's solubility must often be determined experimentally.

Impurities

Impurities in the starting materials can greatly affect the final ceramic. So much as cost is not a limiting factor, the use of clean materials is much preferred.

Microstructure

Of concern is the effect of the starting materials on final microstructure after sintering. There do exist fine and coarse-grained materials. However, other considerations include sinterability, final grain size, shrinkage, porosity, and flaw populations. These properties are often characteristics of the starting materials.

Sinterability

Very fine powders sinter at lower temperatures and produce a finer grain intercept. Sinterability is also influenced by particle shape. Irregular particle shapes result in excess pore coalescence and a decreased sintered density. Blocky shapes pack well and sinter in an orderly fashion.

Firing Shrinkage

Fine powders exhibit higher firing shrinkages for the following two reasons: these powders sinter to higher densities, and as the particle size becomes increasingly fine, surface forces between particles prevent packing to a high green density and result in a larger volume change upon densification.

Flaw Populations

Flaws in the green body greatly influence the fired strength. Strength increases and strength distribution narrows as flaws in the starting powder are removed. This effect is illustrated in Figure 1 as adapted from the literature.

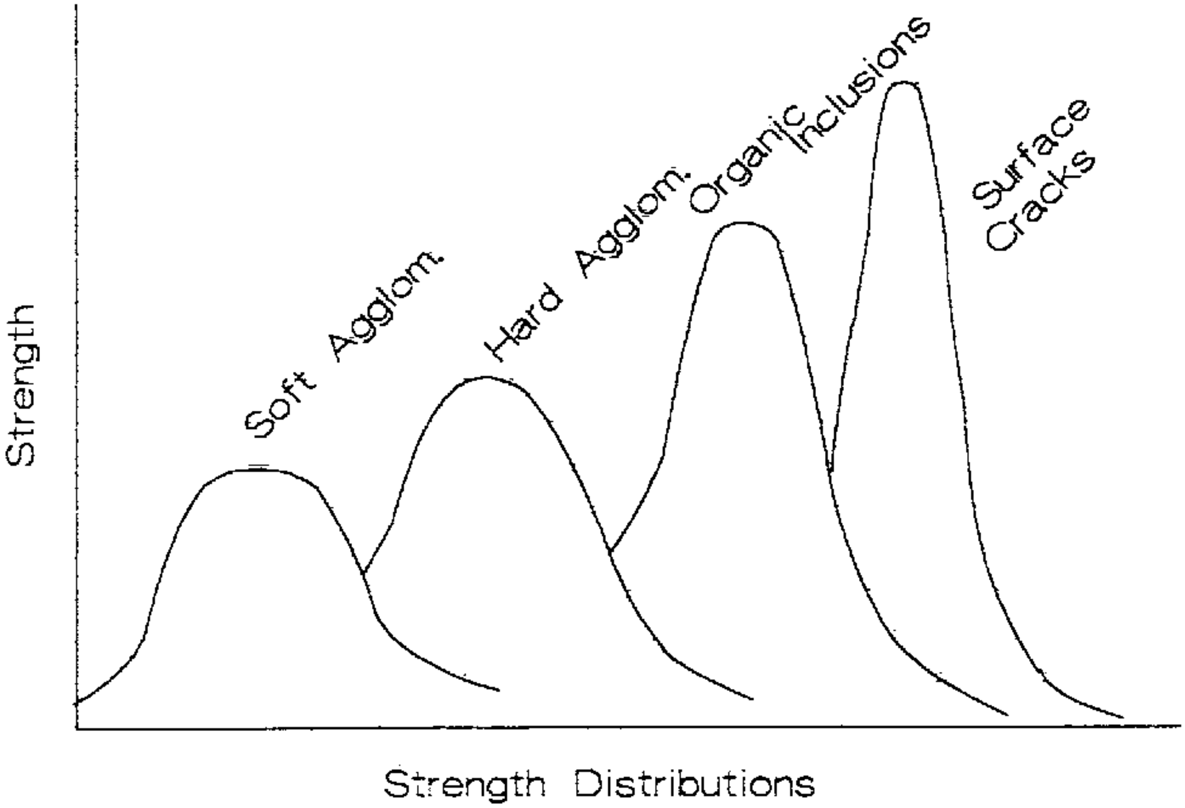

Figure 1: Strength Effect of Removing Flaws. Strength increases as flaws are removed from the starting powder and surface grinding.

EFFECTS OF TEMPERATURE AND PRESSURE ON PROPERTIES

Heat and pressure significantly affect ceramics, as they are materials characterized by strong covalent or ionic bonds. Here is a summary of the most important effects:

1. **Temperature Effect**

Thermal Expansion: Ceramics expand when heated, but at a much slower rate than metals. However, rapid temperature changes can cause thermal shock, which may lead to cracking due to their poor ductility.

Electrical Conductivity: In insulating ceramics, conductivity increases with temperature because the extra energy helps electrons (or ions) move.

Creep: At very high temperatures, ceramics begin to slowly deform under load, a critical phenomenon in gas turbines and engines.

Phase Transformation: The crystal structure may change (such as the zirconia transformation), leading to volume changes that can cause the material to crack.

2. Pressure Effect

Density and Hardness: High pressure (especially during manufacturing processes like heat pressing) eliminates pores, increasing the material's density and mechanical strength. Brittle Fracture: Ceramics are very strong under compression but weak under tension. High pressure can cause the material to crush if it exceeds the grain's load-bearing limits.

Superconductivity: In certain types of advanced ceramics, extremely high pressure can alter the electronic properties and transform the material into a superconductor.

Summary of the Dual Effect: Pressure and heat are often used together in the sintering process to transform powders into highly durable solids by bonding the grains and reducing voids.

EFFECT OF TEMPERATURE ON PROPERTIES:

Properties that are developed in the ceramic are the result of interactions between the starting powder properties, green structure, temperature, and time. Temperature of itself can affect the grain growth, gas desorption, melting, and phase changes such as those found in zirconia systems.

Gas Desorption

Bonding in many ceramics is very strong. When a crystal fractures, the surface bonds are broken and become extremely reactive. Surfaces are very strong absorbents. High-surface-area powders can absorb significant quantities of gases, which are difficult to remove. These types of powders have gained widespread use, making gas desorption an issue.

Observation of Desorption

When a bisque-fired alumina (10m2/g) preform is placed in a vacuum furnace and heated, it desorbs gases. Figure 2 shows the results of this type of experiment. After pumping the system down, the system is closed and the temperature increased by an increment. The pressure is then measured. This process is repeated over the temperature range of significance. An additional run is made without the ceramic as a blank, and these pressure readings are subtracted from the first.

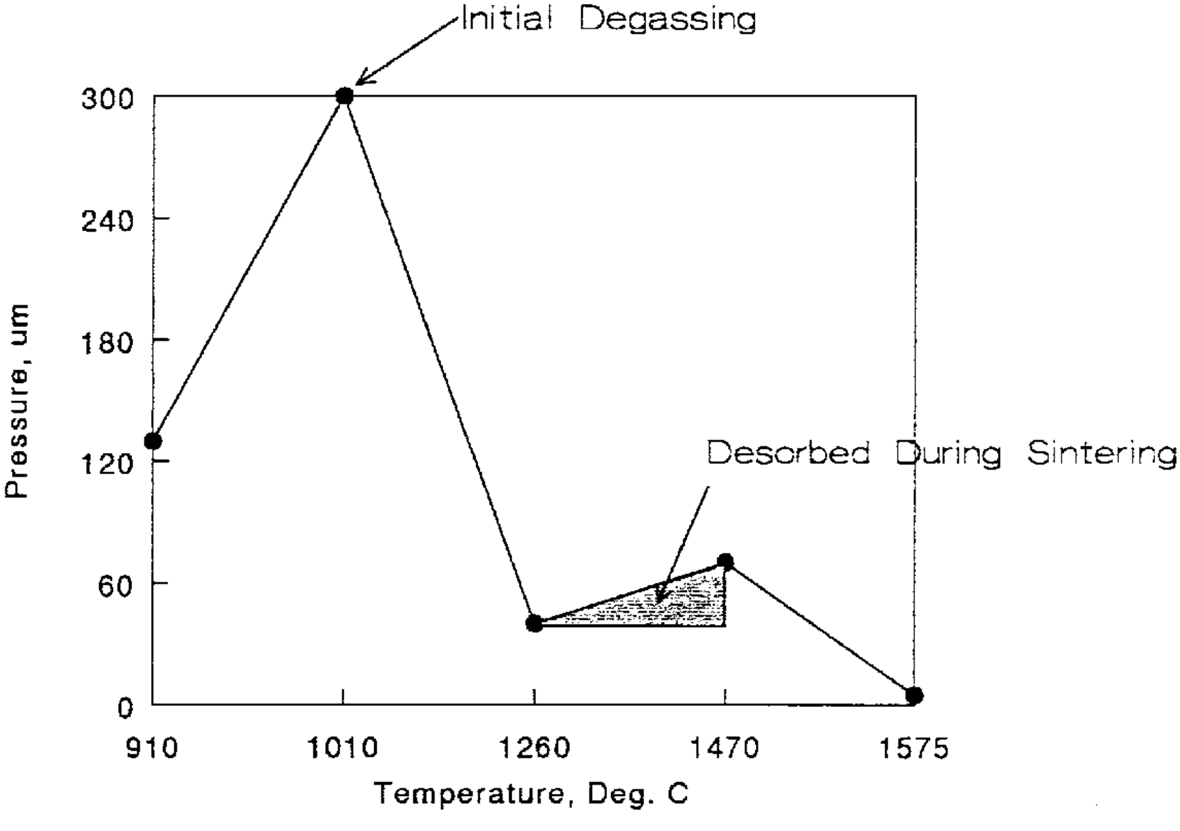

Figure 2: Gas Desorption with Temperature, Alumina. Adsorbed gases are not removed below 1260 °C and can be trapped in the structure.

There is a large burst of desorbed gases as the temperature is increased to 1010 °C. Less gas is evolved at 1260 °C, with a second small burst of desorbed gas when heated to 1470 °C. This last burst of gas is shown by the shading in the figure. The gas amount approximately equaled a monolayer desorbed from the ceramic surface. Thermal gravimetric analyses (TGA) have mistakenly fed the notion that gases are driven off at much lower temperatures such as 400 °C.

Bloating

The problem now becomes one of gases entrapped in the structure.

This problem results from the inability to desorb gases prior to the ceramic sintering to an impervious state. When such a ceramic is reheated, it bloats.

Figure 3 demonstrates bloating in alumina that was hot pressed to several temperatures.

Aluminas hot pressed at 1500 °C and 1600 °C both show decreased density when reheated to 1350-1400 °C. Hot-pressing at 1700 °C produces limited initial bloating but levels off above 1300 °C. It appears that the higher hot-pressing temperature allows the absorbed gases to escape by diffusion while the ceramic is still under pressure in the hot press.

It is important to note the following two factors. When the ceramic part is used at an elevated temperature; it will bloat if sintered at a lower initial temperature. It is likely that the grain boundary contains a monolayer of absorbed gas that is most likely water. In the case of alumina, the boundary bonding may be through OH-OH groups, which, if true, would alter the integrity of the structure. These considerations apply only when the sintering temperature is low enough to entrap absorbed gases, which is not always the case.

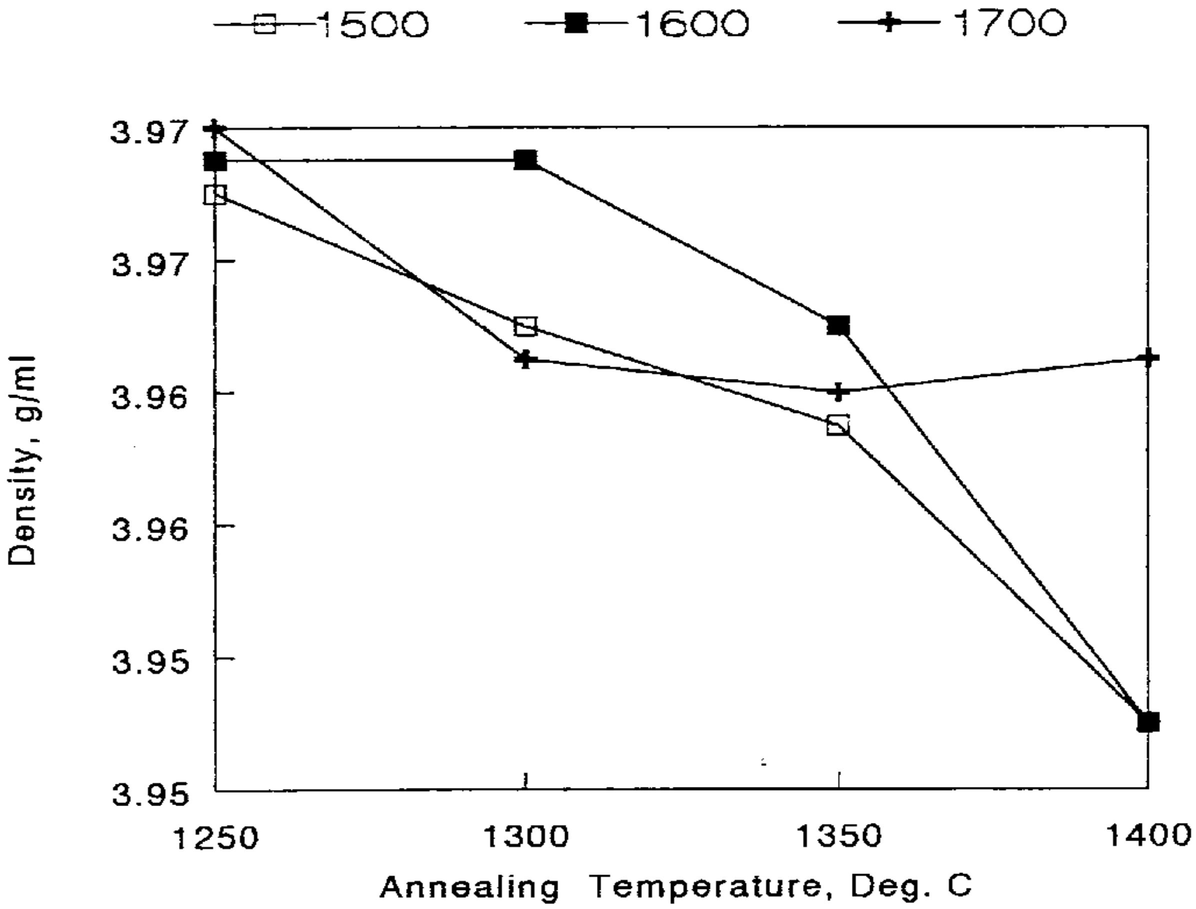

Figure 3 Bloating, Hot-Pressed Alumina. Alumina hot pressed to lower temperatures will bloat when reheated due to entrapped gases.

Decomposition

Temperature can also result in the decomposition of some ceramics, especially when one of the molecules has a higher vapor pressure than the other. Such as

Alumina.

$MgO-ZrO_2$.

SiC/Si_3N_4.

Gas Absorption

The previous discussion showed some of the effects of absorbed gases on microstructure. One must now address the source of these gases.

1. Absorption from the Atmosphere.
2. Absorption in a Kiln.
3. Gases in Graphite.

Effect of Temperature on Grain Size:

It is commonly known that an increase in temperature results in grain growth. This grain growth is beneficial if the desired effect is a decrease in transmitted light scattering. However, grain growth is undesirable for conditions of higher wear resistance. A very important consideration in many ceramics is maintaining pores on the grain boundaries where they can be sintered out. Pores within grains are largely trapped. Control of pore location relates to the rate of grain boundary movement. At least four factors are important: the starting powder, green structure, heating rate, and grain growth inhibitors.

With alumina, MgO is added to control grain growth. When the starting powder is right (i.e., correct sub-micron particle size, high purity, high uniform green density, and deagglomeration), the heating rate is not as critical, but restraints still exist. Figure 4 illustrates the inception of uncontrolled grain growth in alumina without MgO.

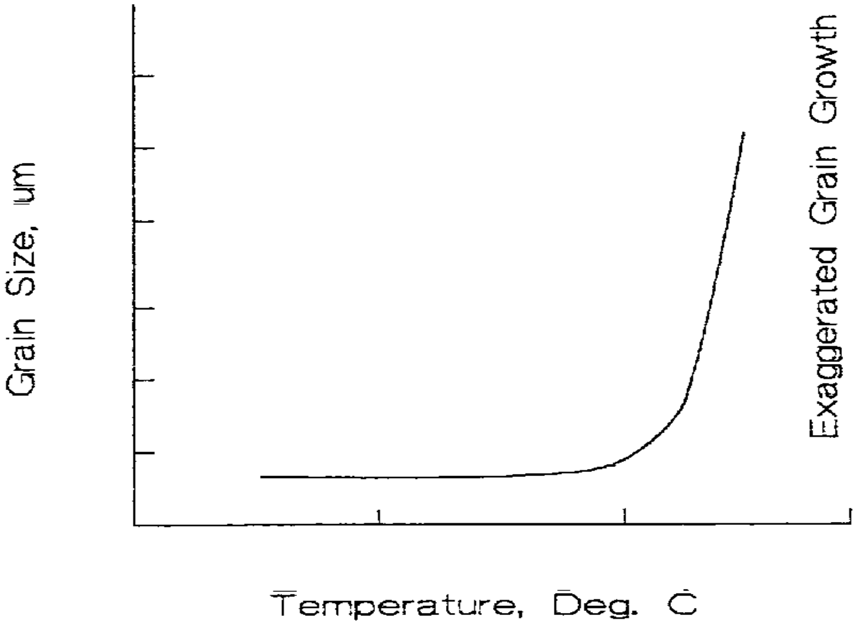

Figure 4: Grain Growth with Temperature, Alumina. Exaggerated grain growth occurs when the temperature reaches a threshold value.

The curve is flat until about 1600 °C where grain growth significantly increases. The examined microstructure reveals that some grains grow at the expense of others and often become faceted. While it is possible that this might increase fracture toughness, it is deleterious to other properties such as strength. To avoid discontinuous grain growth, one should examine the following: the starting powder properties, limited sintering temperature, grain growth inhibitors such as MgO or NiO for alumina, or included second phases that drag on the boundaries as they move.