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BASIC CERAMIC PROCESSING TECHNIQUES

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Basic Ceramic Processing Techniques

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Introduction

Ceramic processing consists of a series of steps each of which is important in producing a ceramic material for a given application. In the technical ceramic field the most important applications of ceramics are in the structural, electronic, and magnetic areas. For illustration purposes two common technical ceramics, aluminum oxide structural ceramics and lead zirconate titinate ferroelectric ceramics will be used. Briefly each processing step will be discussed. These steps include raw material selection, mixing and grinding raw materials, incorporation of binders and lubricants, calcining for compound formation where appropriate, powder forming, and densification of powder compacts at high temperatures.

One must keep in mind that in processing ceramic materials, unlike metals, once the material is produced the properties either mechanical, electrical or magnetic cannot be changed. Metals can be heat treated, mechanically worked, or both to drastically change their mechanical properties.

Raw Material Selection

For many years the ceramic producer did not have raw material sources that could provide materials specifically

for ceramic production. In the aluminum industry one step in the recovery of aluminum oxide from bauxite, a natural occurring hydrated aluminum oxide, produces aluminum oxide. The major use of this material is for abrasives. Many grades were available, but the very small particle size grades (under one micrometer) were very expensive. The increased demand for high purity alumina ceramics and volume of alumina consumed resulted in many alumina producers perfecting alumina powders specifically for high quality ceramic materials at reasonable costs.

The same pattern has been followed in other raw materials. Many chemically prepared and purified raw materials such as TiO_2, ZrO_2, $BaCO_3$, Fe_2O_3, Al_2O_3, BeO, and UO_2 are now available in a series of grades and prices for production of ceramic products.

In many cases the application of a ceramic material in a device does not demand the use of high purity materials. The alumina ceramic manufacturers produce a series of alumina ceramics based on the alumina content. These alumina ceramics vary in Al_2O_3 content from 85 weight % to 99.8 weight %. The lower grades of alumina ceramics can use less pure alumina powders as the starting material and incorporate naturally occurring minerals such as talc to provide MgO and SiO_2 which with Al_2O_3 can form a silicate liquid phase at high temperatures and greatly enhance the densification process in firing. The cost of these ceramics are substantially reduced along with a reduction in high temperature mechanical properties and increased low temperature dielectric loss.

Mixing and Grinding Raw Materials

After raw material selection powders must be prepared for the forming operation. Powder pressing in dies under uniaxial pressure is the most common method of ceramic production for alumina ceramics, piezoelectric and ferroelectric ceramics, and magnetic ferrite ceramics. Slip casting and extrusion are occasionally used. For all these process steps and the latter high temperature densification of the powder agglomerate proper particle size and intimate mixing of dopants, binders and lubricants, and fluxing materials are necessary.

After weighing the moisture free raw materials it is usual to ball mill the mix in an aqueous medium. Common practice is to use high alumina mill jars and high alumina milling media. Where particle size reduction is necessary it is often necessary to use long milling times as shown in Fig. 1. Milling can and frequently does introduce uncontrolled contamination from the milling media and jar. Table I gives some typical data for milling lead zirconate titinate in a high alumina porcelain mill under various conditions using the same jar and pebbles and the same milling time.

Table I

Milling PZT in Al_2O_3

Weight Percent

Impurity	Material as Calcined	Dry Milled	Milled in Water	Milled in Isopropyl Alcohol	Milled in a Plastic Mill by Vibration
Al_2O_3	0.02	0.03	0.50	0.30	0.02
SiO_2	0.01	0.02	0.18	0.08	0.02
MgO	0.001	0.002	0.03	0.03	$<$ 0.001
Ave. Particle Size in Microns	6.4	2.5	1.6	1.6	1.6 - 1.8

As can be seen in the Table a milling procedure that reduces contamination must be followed to produce a high purity ceramic. Typically for controlled composition PZT, the mixing and particle size reduction are done using organic materials for the mill jar and the highest purity Al_2O_3 pebbles available. Time of milling is kept to a minimum.

Binders and lubricants used to provide strength to the formed green body and prevent excessive die wear, respectively, are usually added to the mill. These organic materials are usually selected on the basis of their cost, ash content left during oxidation, and nature of their burn our characteristics (endothermic or exothermic). This area of processing is seldom referred to in the literature as the ceramic producers generally consider such information proprietary.

After milling the suspension of small particles and the mill additions in the milling media are dried by one of a number of processes. Spray drying where small droplets are passed through heated air to form spherical agglomerates is frequently used in large scale production processes. Other techniques employ filtering the suspension then drying the filtrate followed by granulation. Simple evaporation is seldom used because of settling and segregation that may occur. When it is used it is usually followed by a short dry milling step.

Calcining and Compound Formation

In ferroelectric and ferrite materials the desired composition is made by mixing the basic oxides or carbonates, then subjecting those materials to a temperature sufficient

to cause them to interact and form the compound. For example, to form a basic lead zirconate titinate composition. PbO, TiO_2, ZrO_2, and dopant oxides are carefully weighed and mixed then compacted to achieve maximum interparticle contact. At elevated temperatures these basic oxides interact to form $Pb(Zr_xTi_{1-x})O_3$. Because of the difference in solid state diffusion kinetics, the agglomeration of the basic oxide constituents may expand on calcining. This is illustrated in Fig. 2. Due to this reaction sequence large void volumes are created and, therefore, mixtures of oxides cannot be entered directly into a high temperature densification process as will be commented on later.

In the calcining step some densification may occur which develops mechanical strength; therefore, the calcined product must be milled to break up the agglomeration of fine particles. This milling is similiar to that described earlier. Mill additions such as binders and lubricants are added at this step.

Powder Forming

The powder forming processing for ceramics includes slip casting, extrusion, uniaxial die pressing, and isostatic pressing. These processes are used when convential sintering is used. The main incentive of the powder forming process is to achieve the desired compact geometry and density of the powder compact to achieve maximum density in the sintering process. In general, the maximum green density is desired in the powder forming process. This statement should be qualified because in sintering the void volume distribution is important.

A well controlled uniform small pore size, in general, leads to a more uniform sintering and higher density than a wide distribution of pore size.

When powders are compacted in convential uniaxial die pressing density gradients are developed with the maximum density achieved near the outside of the compact especially directly under the plungers of the pressing assembly. These density gradients can lead to anisotropic sintering and develop cracking on heating a powder compact.

Slip casting and extrusion can also lead to anisotropic structures especially when the individual particles are platy or fibrous. These conditions are frequently encountered in alumina ceramics. This preferred orientation introduced in powder forming can lead to anisotropic physical properties in the final ceramic product.

Firing Process

The firing step in the processing of ceramics is the most important. All previous steps have been directed to forming a powder compact as homogenous and uniform as possible and in the desired shape. In the firing process the mechanical, electrical, or magnetic properties are determined through control of the densification and residual porosity, the grain size, secondary phases and their dristribution, and the defect structure produced.

The first step in the firing process is the removal of physically adsorbed water and organic binders and lubricants present in the powder compact. This step is usually accomplished in the general firing cycle, but in some cases it may

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be a separate step. When this step is a separate unit operation, the temperature is usually raised to that necessary to cause neck growth between particles or a secondary phase to develop, sufficient to impart enough strength to the ceramic for handling. The oxidation characteristics of the binder and permeation characteristics of water vapor through the powder compact are extremely important in determining the exact time-temperature program for this operation. Improper heating schedules can cause cracking of the powder compact which can result in residual cracks or regions of nonuniformity in the final product.

When the binder and water removal step is part of the firing process to maximum density then the rate of heating in the low temperature range is important. Some continous tunnel kilns provide for a low temperature soak in the firing process for controlled binder and water removal.

The final firing of a ceramic to achieve the finished product is the most critical step. Many studies have been made on sintering mechanisms for solid state sintering, sintering with a liquid phase present, and sintering under pressure (hot pressing with uniaxial or isostatic load application). Most of these studies directed to determining the mechanisms of sintering and kinetics associated with the process have been isothermal studies.

Practical sintering of ceramic materials is not an isothermal process but involves a time-temperature schedule in which the heating rate and cooling rate play important roles in the process. A recent study at the University of California on the sintering of Al_2O_3 doped with 0.1 weight present MgO for discontinous grain growth control has shown that extensive

densification takes place before the maximum sintering temperature is reached. The observed characteristics are shown in Fig. 3. It is also shown that the maximum densification rate is achieved before the maximum temperature. In this case the sintering is completely in the solid state with Al^{3+} and O^{2-} diffusion rates controlling the mass transport necessary for densification.

The mechanisms that may control sintering include:

1. The diffusion of a vacancy from the region immediately below the surface of a pore to a grain boundary sink. The counter ion diffusion, either cation or anion, can then control sintering kinetics. The diffusion path may be either through the bulk volume of the crystal or along grain boundaries.
2. The solution and subsquent diffusion of ions in a liquid phase developed at high temperatures. In this case either the solution step or the diffusion rate of a specific ion may control the mass transport rate.
3. Plastic deformation by dislocation motion may allow geometric changes of individual small crystalline particles to aid densification. This process can be quite effective when external pressure is applied to a powder compact such as in hot pressing.

In any case of solid state sintering composition and the sintering atmosphere can control the defect concentration and mass transport rate. The sintering rate is also affected by the diffusion path length. Therefore, grain growth will decrease the sintering rate, and this is thought to be responsible for the decrease in densification rate after a given temperature and densify is reached as shown in Fig. 3. If grain

growth can become discontinous (one or more grain grow at a very rapid rate giving very large grains in a fine grain matrix) then pores may be trapped within an individual grain. These pores are almost impossible to remove and lead to reduced maximum density achievable.

Discontinous grain growth can be suppressed by given doping materials. For example MgO added to Al_2O_3 or Nb_2O_5 added to PZT are both effective discontinous grain growth inhibitors. In general, discontinous grain growth inhibitors are those ions that associate with lattice defects through charge compensation. A Mg^{2+} ion substituting for an Al^{3+} ion in a crystal with an excess concentration near a grain boundary will associate with oxygen vacancies and reduce their mobility and subsquent grain boundary mobility.

In firing a ceramic the firing atmosphere may first control defect structure. PZT will develop Pb and O vacancies in its structure depending on the oxygen partial pressure in the sintering atmosphere. In air firing ceramics, gases such as nitrogen may be entrapped in pores, as they become closed.

A back pressure is developed as the pore tries to shrink. This can stop the densification process. Therefore, Al_2O_3 ceramics are sintered in H_2 atmospheres, because the H_2 molecule can easily diffuse out of the pore and along the grain boundary as the pore closes.

Throughout this discussion no mention has been made of the ecomonics of processing except in the selection of raw materials. High quality ceramics for specific applications require processing techniques which in some cases become very expensive. For example, for optically transparent PZT the most successful method of densification is by hot pressing.

Hot pressing is an expensive operation and not easily adapted to volume production. The production of transparent or translucent Al_2O_3 requires H_2 firing atmospheres. This is also expensive and creates some problems in safety. In these cases the product demand must support the more expensive processing.

Acknowledgement

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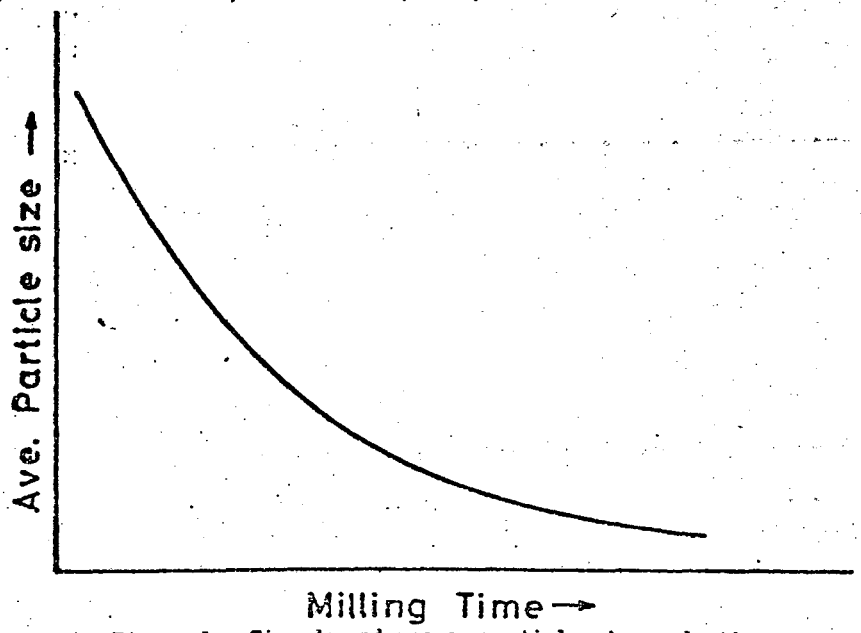
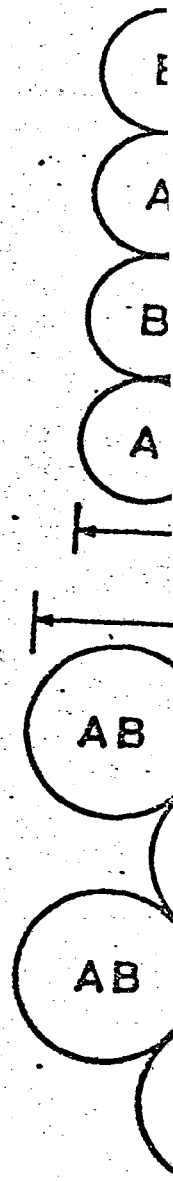


Figure 1. Time dependence on particle size reduction during ball milling.



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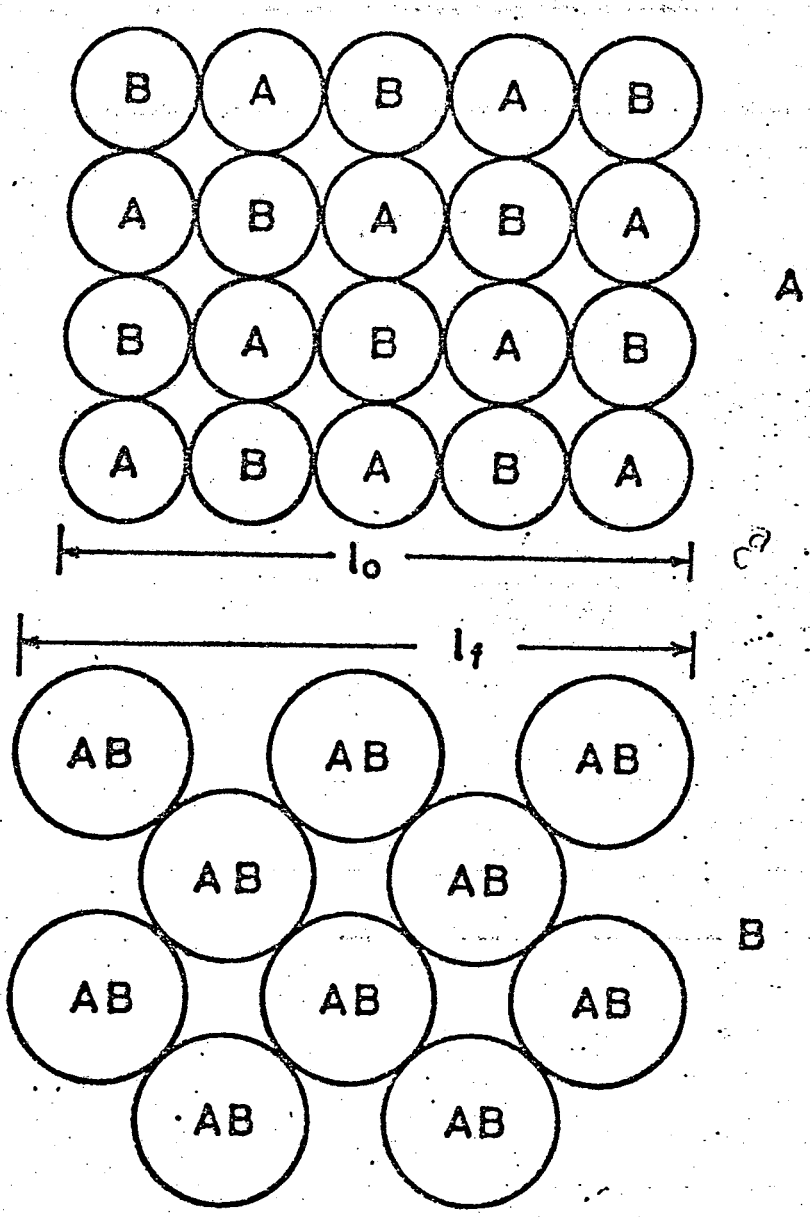

Figure 2. Expansion and void size change on reacting A and B through calcining. It is assumed that A diffuses into B to form the compound AB with little counter diffusion of B.

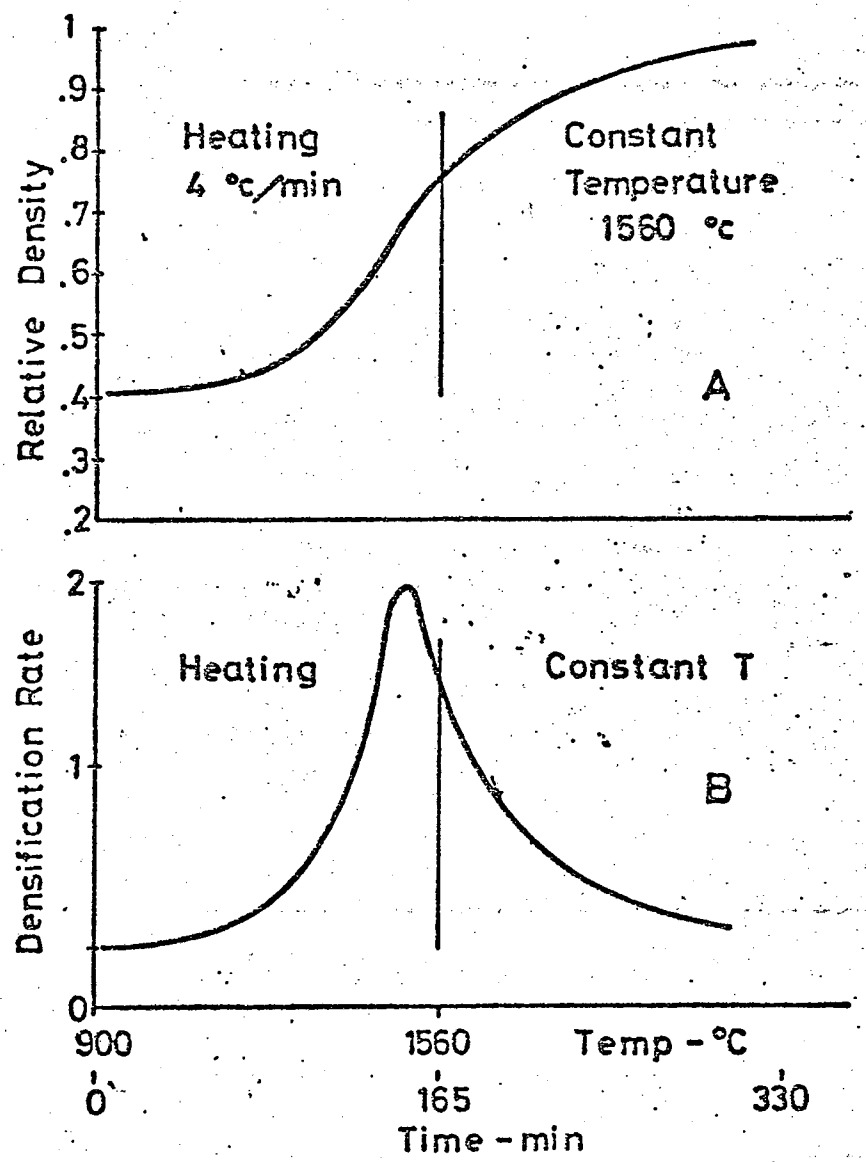

Figure 3. Density (A) and Densification Rate during sintering MgO doped Al_2O_3. Heating rate constant from 900 to 1560 °C at 4 °C/min then isothermal soak at 1560 °C.

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