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CERAMIC PROCESSING

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INTRODUCTION

Ceramics represent a unique class of materials that are distinguished from common metals and plastics by their: 1) high hardness, stiffness, and good wear properties (i.e., abrasion resistance); 2) ability to withstand high temperatures (i.e., refractoriness); 3) chemical durability; and 4) electrical properties that allow them to be electrical insulators, semiconductors, or ionic conductors. Ceramics can be broken down into two general categories, traditional and advanced ceramics. Traditional ceramics include common household products such as clay pots, tiles, pipe, and bricks, porcelain china, sinks, and electrical insulators, and thermally insulating refractory bricks for ovens and fireplaces. Advanced ceramics, also referred to as "high-tech" ceramics, include products such as spark plug bodies, piston rings, catalyst supports, and water pump seals for automobiles, thermally insulating tiles for the space shuttle, sodium vapor lamp tubes in street lights, and the capacitors, resistors, transducers, and varistors in the solid-state electronics we use daily.

The major differences between traditional and advanced ceramics are in the processing tolerances and cost. Traditional ceramics are manufactured with inexpensive raw materials, are relatively tolerant of minor process deviations, and are relatively inexpensive. Advanced ceramics are typically made with more refined raw materials and processing to optimize a given property or combination of properties

(e.g., mechanical, electrical, dielectric, optical, thermal, physical, and/or magnetic) for a given application. Advanced ceramics generally have improved performance and reliability over traditional ceramics, but are typically more expensive. Additionally, advanced ceramics are typically more sensitive to the chemical and physical defects present in the starting raw materials, or those that are introduced during manufacturing.

In general, ceramic manufacturing involves creating fine particle size powders, forming powders into a particulate compact, and heat treating (i.e., sintering) that compact to produce a cohesive body with the desired microstructure and properties for a given application. Because powder systems have a relatively large total surface area for their mass, surfaces and interfaces are very important in ceramic processing. From the perspective of a physical chemist, ceramic processing involves understanding and controlling the physical chemistry of surfaces and interfaces [1,2].

Initially in ceramic powder processing, particle surfaces are created that increase the surface energy of the system. During shape forming, surface/interface energy and inter-particle forces are controlled with surface active additives. Ultimately, surface energy is used to produce a cohesive body during sintering. As such, surface energy, which is also referred to as surface tension, γ, is obviously very important in ceramic powder processing. Surface tension causes liquids to form spherical drops, and allows solids to preferentially adsorb atoms to lower the free energy of the system. And, surface tension creates pressure differences and chemical potential differences across curved surfaces that causes matter to move.

The LaPlace equation, which defines the pressure difference, ΔP, across a curved surface of radius, r,

$$\Delta P = \gamma (1/r_1 + 1/r_2) \tag{1}$$

has been characterized as the fundamental equation of capillarity [1]. In ceramic processing, the pressure associated with surface tension and capillary forces contribute to, among other things, particle clustering (i.e., agglomeration) and rearrangement, to the migration of liquids through pores during mixing, shape forming, and drying, and to pore shrinkage during sintering.

The equilibrium vapor pressure, P, over a curved surface is defined by the Kelvin equation

$$\ln P/P_o = 2\,\gamma\,\Omega\,/\,rkT \qquad (2)$$

where, P_o is the equilibrium vapor pressure over a planar surface, Ω is the molecular volume of the condensed phase, k is Boltzmann's constant, and T is absolute temperature. Because the chemical potential difference, $\Delta\mu$, between a curved and flat surface is related to the vapor pressures over those respective surfaces,

$$\Delta\mu = kT \bullet \ln P/P_o \qquad (3)$$

chemical potential is also related to surface curvature.

$$\Delta\mu = \mu - \mu_o = 2\,\gamma\,\Omega\,/\,r \qquad (4)$$

The chemical potential of a curved surface is extremely critical in ceramic processing. It determines reactivity, the solubility of a solid in a liquid, the rate of liquid evaporation from solid surfaces, and material transport during sintering

This article will describe some of the basic unit processes in ceramic manufacturing, and will touch on the pertinence of the physical chemistry of surfaces in select unit processes. For a more comprehensive review of ceramics and ceramic processing, the reader is referred to other sources [3-5].

POWDER PROCESSING

Ceramic manufacturing involves multiple unit process steps ranging from raw materials beneficiation to finish machining (**Figure 1**). Ceramics are fabricated using raw materials, typically in powder form, that are generally beneficiated to improve their handling and processability. The desired size and shape ceramic component is produced by consolidating powder in a process that generally involves a forming pressure. Ultimately, this powder compact is heat-treated (i.e., sintered) to form a cohesive body.

The fabrication of an alumina spark plug body is a good example of ceramic manufacturing. The manufacturing process begins with an alumina powder (**Figure 2**) comprised of individual alumina particles of the desired size distribution. To enhance densification, precursors of CaO, MgO, and SiO_2 are typically mixed with the alumina powder to produce several weight percent of a glass phase during sintering. This mixture is then transformed into a slurry of ceramic particles dispersed in water, which is subsequently granulated with an organic binder by spray-drying. Spray drying produces larger clusters of particles called agglomerates or granules that have improved powder flow, packing, and formability (**Figure 3**). These granules are then pressed and machined to produce a powder compact of the desired size and shape that is held together by the organic additives. Finally, this powder compact is sintered to produce a dense ceramic spark plug body (**Figure 4**). The mechanical and electrical properties of this body are determined by the microstructure of the polycrystalline alumina ceramic produced on sintering (**Figure 5**).

There is unquestionably a substantial engineering component in manufacturing ceramics. There is also a very critical scientific component that involves understanding and controlling the physical chemistry of surfaces. Not only are a number of different unit process steps required to manufacture a ceramic, but each unit process has it's own set of requirements for optimization. Often, the requirements to optimize one step are diametrically opposed to those for another unit processes. This necessitates compromise to optimize the complete manufacturing process. For example, while a fine particle size powder provides a high surface area and driving force for sintering, electrostatic attraction and van der Waals forces promote agglomeration of fine particles and make them difficult to mix, pack, and compact. As a compromise, a practical lower limit of ~0.1 μm diameter particles, is typical in advanced ceramic powder processing.

Raw Materials

Ceramic processing generally starts with ceramic powders that range from relatively impure, naturally occurring clays, to ultra-high purity, controlled morphology powders. Inexpensive, mined raw materials are typically used to manufacture traditional, high volume production, ceramics [6-12]. Chemically synthesized ceramic powders, which are often considerably more expensive, are used to manufacture high-cost, lower-volume, advanced ceramics [13-20].

Naturally occurring ceramic raw materials such as silica ($Si0_2$, or quartz), silicates (e.g., talc) and aluminosilicates (e.g., clays) are generally mined from the earth's surface. In contrast, nanometer size, controlled chemistry ceramic powders are produced from high-purity, specialty chemicals. Precipitation of solids from liquid solutions is one example. Precipitation occurs by a combination of nucleation and growth, both of which occur to lower the free energy of the system. And the system's desire to minimize its surface energy per unit volume determines the shape of the precipitate. Most powders used in the manufacture of advanced ceramics fall somewhere between these two extremes. For example, reasonably pure ceramic powders can be formed by reacting constituent oxide powders and/or salts at an elevated temperature (i.e., calcining). Barium titanate, $BaTiO_3$, which is used to make capacitors in solid-state electronics, can be produced by mixing $BaCO_3$ with TiO_2 and calcining. High surface area, fine powders promote rapid and complete reaction of the constituent powders to produce the desired compound.

Beneficiation

Beneficiation is the process or processes whereby the chemical and/or physical properties and characteristics of a raw material are modified to make it more processable. Particle size reduction (i.e., comminution) using mechanical energy may be the most common process [21-28]. Crushing, grinding, and/or milling create new surfaces by breaking down aggregates (i.e., clusters of tightly bound particles) and by fracturing particles. Comminution produces the desired size distribution powder for subsequent processing.

After comminution, soluble impurities either inherent to the raw materials or introduced during processing can be extracted by washing (e.g., with water) followed by filtration [6, 23]. Chemical leaching and magnetic separation are also used to purify raw materials. In a more specialized process, a frothing agent can be used to promote differential adsorption of impurity particles onto gas bubbles to separate out the desired product [23].

Granulation

In dry powder processing, after the desired particle size and chemistry are obtained, the powder is generally granulated. Powders comprised of micrometer size particles are difficult to handle due to inter-particle forces. Granulation transforms individual particles into agglomerates with controlled size, shape, and strength, to improve the flow, packing, and compaction behavior of powders in ceramic processing [29-31]. Granules are formed by spraying a liquid or a binder solution directly into a tumbling powder, or by spray drying a slurry into a heated chamber. In the former, granules form under the influence of the capillary forces between the liquid-solid (particle) interfaces. In spray drying, a combination of (liquid) surface tension and interparticle forces produce ~50-300 μm diameter granules. Due to liquid surface tension, the atomization of a slurry produces spherical droplets that subsequently dry to form spherical granules. Capillary forces hold the individual particles together within the granule during the drying, while van der Waals forces and bonds from the organic additives adsorbed onto particle surfaces hold the dry granule together.

Forming Additives

Immediately prior to, during, and/or immediately following granulation, forming additives or processing aids are commonly added to a ceramic powder to enhance processing [32-37]. Organic additives adsorb onto the surfaces of ceramic particles to modify surface energy and particle-particle interactions. Two common additives used in ceramic processing are binders and lubricants. Organic binders, which are also referred to as coagulants and flocculants, are polymer molecules or colloids that adsorb onto particle surfaces and promote interparticle bridging (i.e., flocculation). The main purpose of a binder is to provide strength to the powder compact after shape forming, which may be necessary for subsequent handling and/or green machining. Binders are used extensively in dry powder pressing operations, and are also added to extrusion bodies and to pastes.

Lubricants are added to lower interfacial frictional forces between individual particles, and/or between particles and forming die surfaces to improve compaction and ejection (i.e., extraction of the pressed compact from the forming die). Individual particle surfaces can be lubricated by an adsorbed film that produces a smoother surface and/or decreases interparticle attraction. Forming (die) surfaces can be lubricated by coating with a film of low viscosity liquid such as water or oil.

SHAPE FORMING

Ceramic forming typically involves using pressure to compact and mold particles to the desired size and shape. Ceramics can be formed from slurries, pastes, plastic bodies (i.e., like a stiff mud), and from wet and dry and powders.

Slurries

In preparation for the shape forming process, ceramic particles can be dispersed in a liquid. The dispersion of solid particles in a liquid is known as a slurry, and is often referred to as a suspension, or a dispersion. Forming a slurry involves; 1) wetting the solid particle surface with the liquid (i.e., replacing solid-vapor interfacial area with solid-liquid interfaces), 2) breaking down agglomerates, and 3) controlling particle surface charge to prevent flocculation or reagglomeration [38-42]. To optimize dispersion and stability, dispersants, also known as deflocculants or anticoagulants, are often added to slurries [33,36]. Deflocculants prevent dispersed particles from reagglomerating in a slurry by keeping particle-particle separation distances sufficiently large such that the short range van der Waals attractive forces that will hold particles together are negligible. Particle separation is maintained by the steric effect of the preferential adsorption of large deflocculant molecules on the particle surfaces. Electrostatic stabilization is achieved through the use of the electrical double layer that forms around particles such that neighboring particles are repelled from one another by like (negative or positive) surface charges. Deflocculation by electrostatic stabilization is common in clay slurries as well as with ceramic particles dispersed in polar liquids (e.g., water).

The use of acids and bases to control inter-particle forces in oxide (ceramic)-water suspensions is an example of electrostatic stabilization. Hydroxylated oxide surfaces react with H^+ (acid) or OH^- (base) by surface ionization to become positively charged (low pH) or negatively charged (high pH), respectively. The like-charged particle surface layers repel neighboring particles and stabilize the solution. A stable dispersion is produced by progressively adding acid or base to a system to increase the particle surface charge such that the long-range electrostatic repulsive forces dominate over the short-range van der Waals attractive forces. Conversely, an oxide slurry can be induced to flocculate by adjusting the system pH to the point where there is no net charge on a particle's surface. The pH at which this occurs is defined as the point of zero charge (PZC) for the oxide. At the PZC, the electrostatic repulsive forces are eliminated and the van der Waals attractive forces take over causing flocculation. Surfactants or wetting agents offer another means to improve dispersion in a slurry. By reducing the surface tension of a liquid, a wetting agent decreases the solid-liquid interfacial energy, making it more favorable for the liquid to coat the solid particles. A low surface tension surfactant also makes a good antifoam agent.

Casting

Slurry or slip casting provides a relatively inexpensive way to fabricate uniform thickness, thin wall, or large cross section shapes [43-48]. For slip casting, a slurry is first poured into a porous mold. Capillary suction then draws the liquid from the slurry to form a higher solids content, close-packed, leather-hard cast on the inner surface of the mold. In a fixed time, a given wall thickness is formed, after which the excess slurry is drained.

Electrophoretic deposition (EPD) is another method of casting slurries. EPD is accomplished through the controlled migration of charged particles under an applied electric field. During EPD, ceramic particles typically deposit on a mandrel to form coatings of limited thickness, or thin tubular shapes such as solid β'''- Al_2O_3 electrolytes for sodium-sulfur batteries.

Drying

After casting, the residual liquid in the ceramic part must be removed by drying [49-54]. It is important to achieve relatively uniform drying throughout the body to avoid excessive differential (capillary) stresses and stress gradients that can result in drying cracks (i.e., like those formed in a mud puddle), and warping (i.e., like that seen in lumber on drying). Air drying by convection and conduction is the most common means of drying ceramic ware, whereby drying occurs by liquid evaporation at the drying front. Initially, the drying front starts at the ware surface and then moves into the part. During drying, liquid migrates to the drying front by capillary flow, chemical diffusion, and/or thermal diffusion at a rate determined by the permeability of the ware. The size of the porosity in the ceramic body, the viscosity and surface tension of the liquid, and the moisture gradient from inside the body to the drying front determine the permeability. When liquid migration cannot keep pace with the evaporation process, the drying front moves from the surface into the body, where drying continues by evaporation from the menisci of the liquid within the pores. Large pores and interstices are emptied in preference to smaller pores, and the large capillary stresses produced as the menisci recede into fine pores can result in cracking. The finer the particles, the greater the drying shrinkage, and the greater the capillary stresses during drying.

Stresses during drying can be minimized by controlled humidity drying, by supercritical drying, or by freeze drying. Controlled humidity drying utilizes a high humidity atmosphere during the critical, initial stage of drying to maintain a liquid film on the (solid) surface of the ware (i.e., a solid-liquid interface). Supercritical drying is accomplished by heating ware under pressure in an autoclave until the liquid becomes a supercritical fluid (i.e., both a liquid and a vapor simultaneously), after which drying can be accomplished by isothermal depressurization to remove the vapor. Supercritical drying is often used to avoid generating catastrophic capillary stresses during the drying of fine pore materials such as gels. Freeze drying makes use of freezing and sublimation to minimize drying stresses due to capillarity. In freeze drying, the temperature of the ware is initially decreased to below the freezing point of the liquid. Then the pressure is reduced to transform the frozen liquid to a vapor and remove it. Freeze drying is commonly used to make powders that are not aggolmerated.

Powder Pressing

Powder pressing may be the most common method of forming ceramic components [55-59]. Dry pressing, also referred to as mechanical pressing is an economical, yet versatile technique for fabricating small, relatively simple shape powder compacts. Automated dry pressing, which is used extensively in the production of pharmaceutical tablets, is capable of producing 5000 ceramic parts per minute. Dry pressing involves compacting a, typically granulated, ceramic powder between two plungers in a die cavity. Friction between the powder and the die walls must be controlled during forming to minimize pressing pressure gradients that can create defects in the form of density gradients and/or cracking in a pressed powder compact. Friction can be controlled by using lubricants during forming, or through the design of the die (i.e., materials and geometry).

THERMAL PROCESSING

Generally, the last step in ceramic component manufacturing is thermal processing [60-63]. This is the stage where the weakly bound particulate body produced during shape forming is heat-treated to produce a cohesive body with the desired properties for its end use application. Thermal consolidation, which is more commonly referred to as "firing," typically involves two steps, burnout and sintering. Generally, both are accomplished in a single firing process with burnout preceding sintering.

Burnout

The burnout stage involves eliminating the organic processing aids and any residual organic impurities or water prior to sintering [60-63]. Minor concentrations of residual liquid used in forming, and physically adsorbed moisture on particle surfaces can be eliminated on heating to ~200°C. Most organic binders used in ceramic forming are physically adsorbed onto particle surfaces, and can be burned out by heating to ~500°C. Clays such as kaolin must be heated to 700°C to liberate the water of crystallization and produce the desired dehydrated aluminosilicate phase for subsequent processing. Decomposition of constituents such as sintering aids, which may be added in the form of a salt precursor, may require temperatures up to ~900°C. Temperatures in excess of 1000°C may be required to completely eliminate chemically adsorbed water on fine particle surfaces.

Sintering

Sintering involves the densification and microstructure development that transforms the loosely bound particles in powder compact into a dense, cohesive body [60-73]. The end-use properties of a finished ceramic are largely dependent on the degree of densification achieved during sintering, and on the microstructure produced; consequently, sintering is one of the most critical steps in ceramic processing. Sintering, which is often considered to be synonymous with densification, is usually accomplished by heating a powder compact to approximately 2/3 of its melting temperature for a given time. Sintering can also occur by subjecting a powder compact to externally applied pressure, or heat and pressure simultaneously (e.g., hot pressing and hot isostatic pressing). A ceramic densifies during sintering as the porosity (i.e., void space) between solid particles is reduced in size with time. Concurrently, the cohesiveness of the body increases as inter-particle contact (i.e., grain boundary) area increases during sintering.

driving force for sintering

Ceramic powder compacts sinter as a result of the thermodynamic driving force to minimize the Gibbs' free energy, G, of a system [61-64, 74]. This includes minimizing volume, interfacial, and surface energy in the system. In a powder compact, excess free energy is present primarily in the form of the surface or interfacial energy (i.e., liquid-vapor and/or solid-vapor interfaces) associated with porosity. Under the influence of elevated temperature and/or pressure during sintering, atoms migrate to thermodynamically more stable positions within a powder compact. Material transport is driven by the chemical potential difference that exists between surfaces of dissimilar curvature within the system. Physically, in a particulate system, atoms or ions move from higher energy convex (i.e., as viewed from the particle center out) particle surfaces to lower energy concave particle surfaces to decrease the curvature and chemical potential gradients in the system.

Material transport can occur by solid-state, liquid-phase, and/or vapor-phase mechanisms. For polycrystalline ceramics, material transport commonly occurs as ions diffuse through the volume, along grain boundaries (i.e., particle-particle intersections), and on particle surfaces (**Figure 6**). Additionally, ions can vaporize from, and subsequently re-condense onto particle surfaces (i.e., evaporation-condensation). A powder compact will densify (i.e. undergo volume contraction) when material transport occurs in a manner that allows particle centers to approach during sintering. Material transport by volume and grain boundary diffusion can result in densification. Material transport that changes the geometry of the system without densification is termed coarsening. Grain growth is perhaps the most prevalent form of coarsening during sintering. Coarsening can occur when material is transported by volume diffusion, surface diffusion, or evaporation-condensation.

densification and microstructure development

Microstructurally, material transport during sintering manifests itself as interparticle pore shrinkage, grain boundary formation, a decrease in the total volume of the system (i.e., densification), and an increase in the average size of the particles that make up the compact (i.e., grain growth) [61-64]. Interparticle contacts flatten, the curvature within the system decreases, and the surface area and free energy of the system decrease during sintering

The ideal sintering process can be divided into three basic stages [75]. Initially, material is transported from convex particle surfaces to the pore-grain boundary intersection to form necks between adjacent particles. As this occurs, grain boundaries grow to create a three-dimensional array of approximately cylindrical, interconnected (i.e., continuous) pore channels at three grain junctions throughout the compact. These pore channels shrink in diameter during intermediate-stage sintering. Ultimately, because of Rayleigh instability (i.e., the critical "cylinder" length to diameter ratio), the channels pinch off to form approximately spherical, isolated (i.e., closed) pores at four grain junctions within the ceramic matrix. The radial shrinkage of closed pores and the growth of larger grains at the expense of smaller ones constitute the final-stage sintering.

Sintering phenomena is generically similar in real powder compacts; however, factors including surface energy anisotropy and packing heterogeneities in real systems can contribute to heterogeneous (i.e., non-uniform) densification and microstructure development. To circumvent this problem, minor concentrations of select chemicals, referred to as sintering aids or dopants, are commonly added prior to sintering. These chemical impurities preferentially segregate to high energy crystallographic planes to decrease the crystalline anisotropy in the system to provide improved control over microstructure development during sintering. MgO-doped Al_2O_3 is the classic example in ceramics [71]. Impurity segregation to high energy grain boundaries also will produce lower energy interfaces that reduce the overall driving force for material transport during sintering.

solid state sintering

Ceramics can be densified by solid-state [71-73,75], liquid-phase (LPS) [76], and viscous [77] sintering. Solid-state sintering refers to the process whereby densification occurs by solid-state diffusion controlled material transport. Densification occurs as higher energy solid-vapor (i.e., pore) interfaces are replaced by lower energy solid-solid (i.e., grain boundary) interfaces. The change in free energy associated with the elimination of porosity, which drives densification, can be approximated by

$$dG = \gamma_{ss} dA_{ss} - \gamma_{sv} dA_{sv} \tag{5}$$

After the pore surfaces are eliminated and densification is complete, grain growth can further reduce the free energy of the system by reducing the amount of high energy solid-solid interfacial area. The change in free energy associated with the elimination of particle-particle interfaces, which drives grain growth, can be approximated by

$$dG = - \gamma_{ss} dA_{ss} \tag{6}$$

Because densification occurs via the shrinkage of thermodynamically unstable pores, densification and microstructure development can be assessed on the basis of the dihedral angle, θ, formed as a result of the surface energy balance between the two solid-vapor and one solid-solid interface at the pore-grain boundary intersection [61, 78-80],

$$\theta = 2\cos^{-1}\left(\frac{\gamma_{ss}}{2\gamma_{sv}}\right) \tag{7}$$

where γ_{SS} and γ_{SV} are the solid-solid and solid-vapor interfacial energies, respectively (**Figure 7**). Pore shrinkage and densification are favored by a dihedral angle that is greater than the geometric dihedral angle, ψ, of the regular polyhedron whose number of sides equals the coordination number of the pore. Theoretically, for the ideal four-sided pore present during final stage sintering, θ must be greater than 70.4°, the geometric dihedral angle for a tetrahedron, to achieve 100% theoretical density during sintering. A larger dihedral angle will be required to be eliminated larger pores surrounded by more grains formed as a result of packing defects. The larger the dihedral angle, the larger the inter-granular pores that can be eliminated during sintering and the greater the surface tension driving force for pore shrinkage. Thermodynamics and/or kinetics limit the shrinkage of pores trapped within grains (i.e., intra-granular porosity) and pores above a critical size [78-80].

liquid-phase sintering

To promote faster densification at lower temperatures, relatively small concentrations of chemical additives referred to as sintering aids are commonly used to create a liquid phase during sintering. Traditional liquid-phase sintering (LPS) involves heating and melting crystalline solids to form a eutectic liquid during sintering [63,76]. The requirements for LPS are that the liquid wet the solid particles, there is sufficient liquid present, and that the solid is soluble in the liquid. The concentration of the liquid and the solubility of the solid in the liquid (i.e., reactivity) increase dramatically with increasing temperature above the eutectic temperature.

LPS is significantly more complex than solid-state sintering in that there are more phases, interfaces, and material transport mechanisms to consider. In general, densification will occur as long as it is energetically favorable to replace liquid-vapor (lv), solid-solid (ss), and solid-vapor (sv) interfaces with solid-liquid (sl) interfaces during sintering.

$$dG = \gamma_{sl}dA_{sl} - (\gamma_{lv}dA_{lv} + \gamma_{ss}dA_{ss} + \gamma_{sv}dA_{sv}) \tag{8}$$

Densification during LPS occurs in three stages. Initially, liquid forms at particle intersections and redistributes throughout the particulate mass under the influence of the capillary action. Shear stresses due to the capillary pressure imbalance on different particles (e.g., different size particles) contribute to particle rearrangement to improve packing and contribute to initial stage densification. Solution-precipitation controls densification during intermediate-stage sintering. Material dissolves from higher energy, convex particle surfaces and migrates to lower energy, pore surfaces where it precipitates. This process is sometimes referred to as grain accommodation, because individual grains will actually change shape to fill void space. Densification by solution-precipitation continues until a rigid, three-dimensional skeletal structure is formed. The transition to final-stage LPS occurs when closed pores are formed at a compact relative density of ~90%. Final stage LPS, as with solid-state sintering, is characterized by the shrinkage of isolated pores and by grain growth.

In liquid-phase sintering, densification and microstructure development can be assessed on the basis of the liquid contact or wetting angle, ϕ, formed as a result of the interfacial energy balance at the solid-liquid-vapor intersection as defined by the Young equation,

$$\phi = \cos^{-1}\left(\frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}\right) \tag{9}$$

where γ_{sl} and γ_{lv} are the solid-liquid and liquid-vapor interfacial energies, respectively (**Figure 8**). A low contact angle favors liquid wetting of particle surfaces and densification during LPS. Theoretically, ϕ must be less than 60° to achieve 100% of theoretical density.

pressure sintering

Pressure sintering employs the simultaneous use of both pressure and temperature during sintering to effect densification. Externally applied pressure on a powder compact increases the compressive stress at particle contacts, increasing the chemical potential gradient and the driving force for material transport relative to conventional sintering [63, 79-80]. During conventional solid-state sintering, the driving force (DF) for final-stage pore closure at any given time, t, is determined by the surface energy, γ_{SV}, of the sintering material and the radius, r, of the pore.

$$DF(\gamma)_t = 2\,\gamma_{sv} / r_t \qquad (6)$$

During pressure sintering, inter-particle compressive stress, approximated by the externally applied stress, σ_a, normalized by the relative density of the compact, ρ, supplements the surface tension driving force for pore shrinkage.

$$DF_t = DF(\gamma)_t + \sigma_a / \rho \qquad (7)$$

As such, under an externally applied pressure, a powder compact can densify faster and/or at a lower temperature during sintering. Pressure sintering is generally used to densify materials that are difficult or impossible to densify conventionally, and to produce dense, fine grain size ceramics without the use of sintering aids. Additionally, the increased driving force for material transport and densification makes it possible to eliminate larger pores during pressure sintering, which can contribute to improved performance and reliability.

sintering atmosphere

The sintering atmosphere plays an important role in determining how a material densifies, the ultimate density achieved, and the end-use properties of the finished ceramic [63]. Particularly in complex electronic ceramics like lead zirconate titanate, where the phases present during and after sintering are strongly dependent on oxygen stoichiometry, sintering atmosphere can determine if the system densifies by solid-state or liquid-phase sintering, and what the resultant electrical properties are [61]. Additionally, if gas from the sintering atmosphere becomes trapped in closed pores during final-stage sintering and cannot readily diffuse through the system, it will impede and ultimately limit densification [81]. The pressure, P, of the gas trapped within a closed pore will counteract the surface tension driving force to shrink the pore during sintering.

$$DF_t = DF(\gamma)_t - P_t \tag{8}$$

Trapped gas in closed pores often limits densification when sintering with a liquid or viscous (glass) phase because rapid material transport through the liquid often results in pore closure early in the sintering process.

SUMMARY

The manufacture of a ceramics starts with the constituent raw materials, and carries through thermal consolidation. Intermediate processing steps include raw material beneficiation, shape forming, and pre-sinter thermal processing. Surfaces are created, modified, and eliminated during ceramic powder processing. Optimizing ceramic manufacturing requires understanding and controlling the physical chemistry of surfaces and interfaces during the various unit process steps. The control and utilization of surface energy and surface curvature are critical. Surface tension creates pressure gradients that contribute to the agglomeration and rearrangement of particles in powders, to the migration of liquids during mixing, shape forming, and drying, and to pore shrinkage during sintering. Chemical potential gradients associated with surface curvature determine the solubility of particles in liquids, control the rate of evaporation from solid surfaces, and drive material transport during sintering. In combination with a strong engineering component, robust ceramic processing requires understanding and controlling the physical chemistry of surfaces.

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FIGURES

Figure 1. A flow chart summarizing the ceramic design and manufacturing process

Figure 2. A scanning electron micrograph showing the individual particles in a polycrystalline alumina powder.

Figure 3. A scanning electron micrograph of the spherical alumina granules produced by spray drying a ceramic slurry. The granules are comprised of individual alumina particles, sintering additives, and an organic binder.

Figure 4. A commercial spark plug with its electrically insulating ceramic body comprised of alumina and glass (white portion).

Figure 5. Scanning electron micrographs showing the microstructure of an alumina ceramic spark plug body a) fracture surface, and b) polished and thermally etched cross section.

Figure 6. The classic two-particle sintering model illustrating material transport and neck growth at the particle contacts resulting in coarsening (left) and densification (right) during sintering. Surface diffusion (a), evaporation-condensation (b), and volume diffusion (c) contribute to coarsening, while volume diffusion (d), grain boundary diffusion (e), solution-precipitation (f), and dislocation motion (g) contribute to densification.

Figure 7. An illustration of the equilibrium dihedral angle, θ, formed by the balance of interfacial energies at a pore-grain boundary intersection during solid-state sintering.

Figure 8. An illustration of the equilibrium contact (i.e. wetting) angle, ϕ, formed by the balance of interfacial energies for or a liquid (sessile) drop on a flat solid surface.

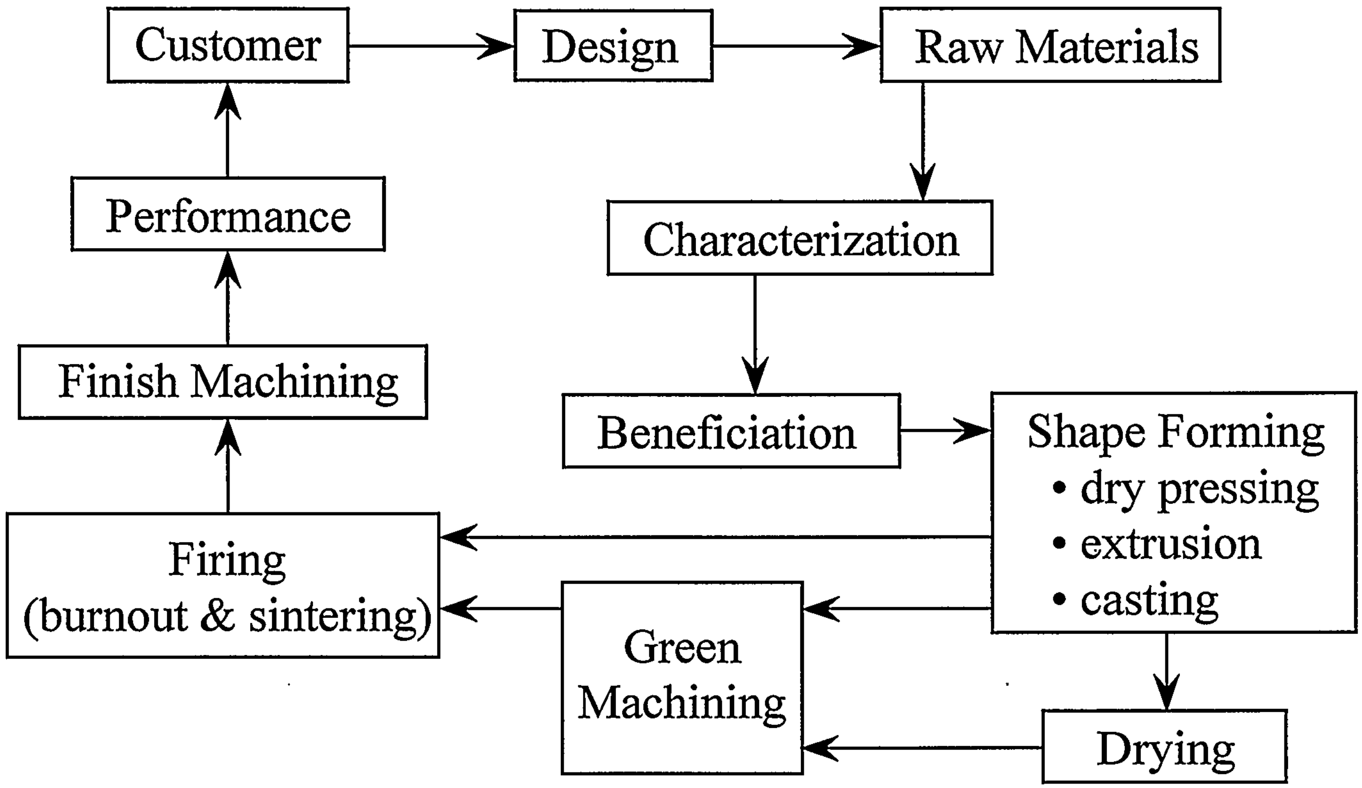
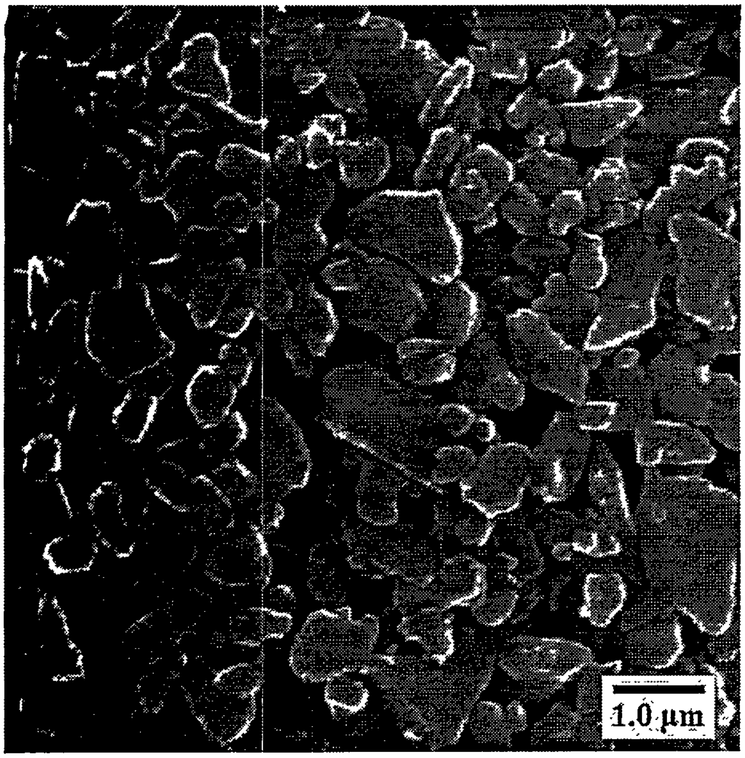

Customer
Design
Raw Materials
Performance
Characterization
Finish Machining
Beneficiation
Shape Forming
• dry pressing
• extrusion
• casting
Firing
(burnout & sintering)
Green
Machining
Drying

Fig 1


1.0 µm

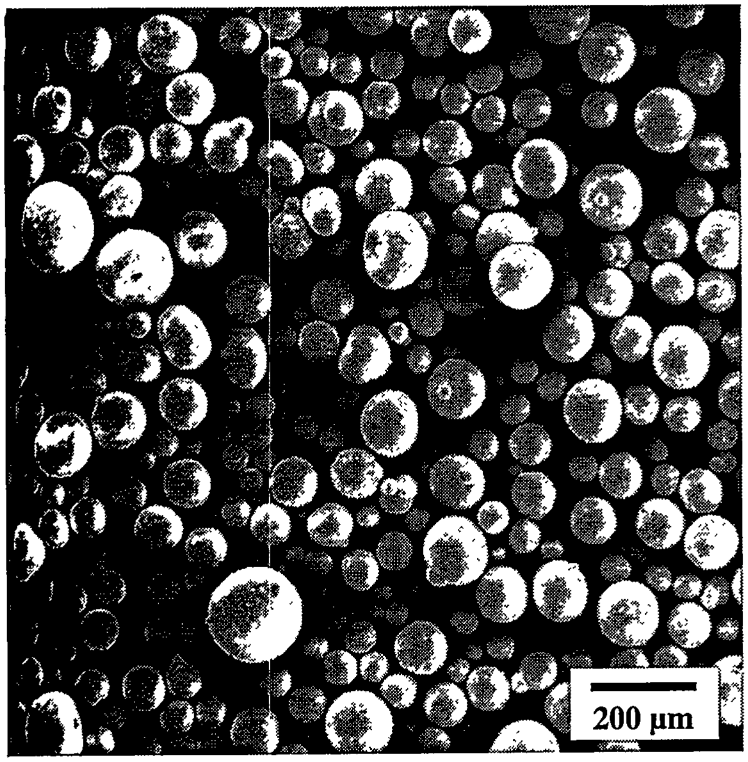


Fig 3

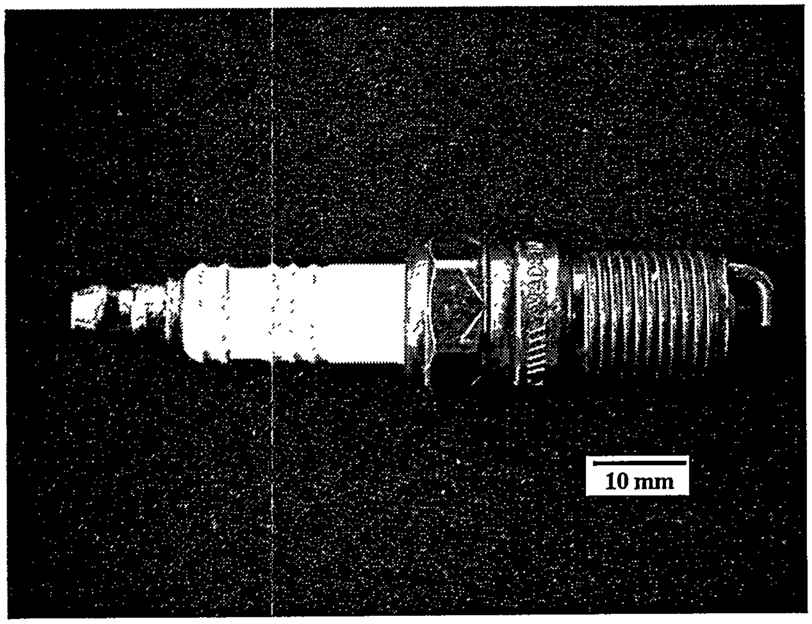


Fig 4

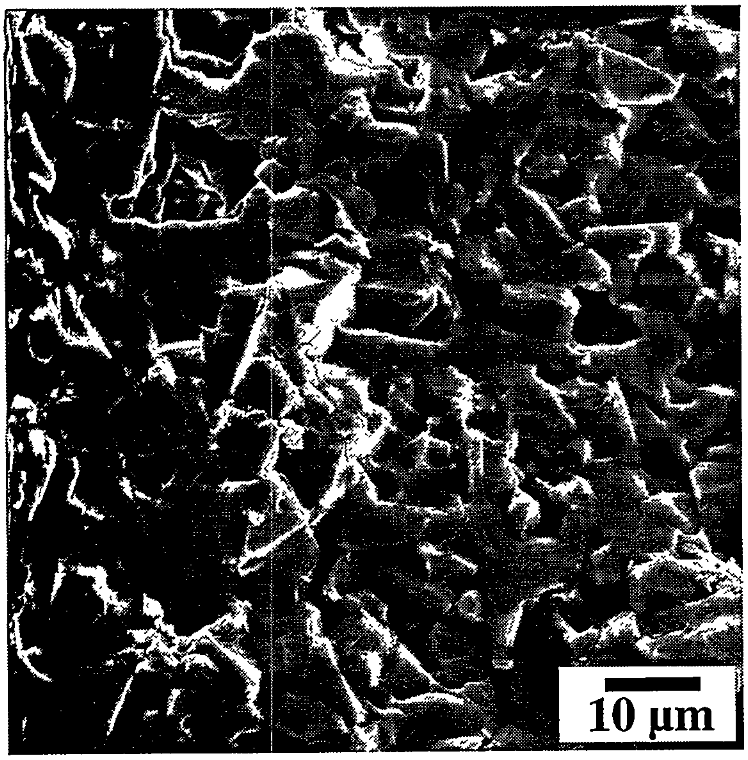


Fig 5A

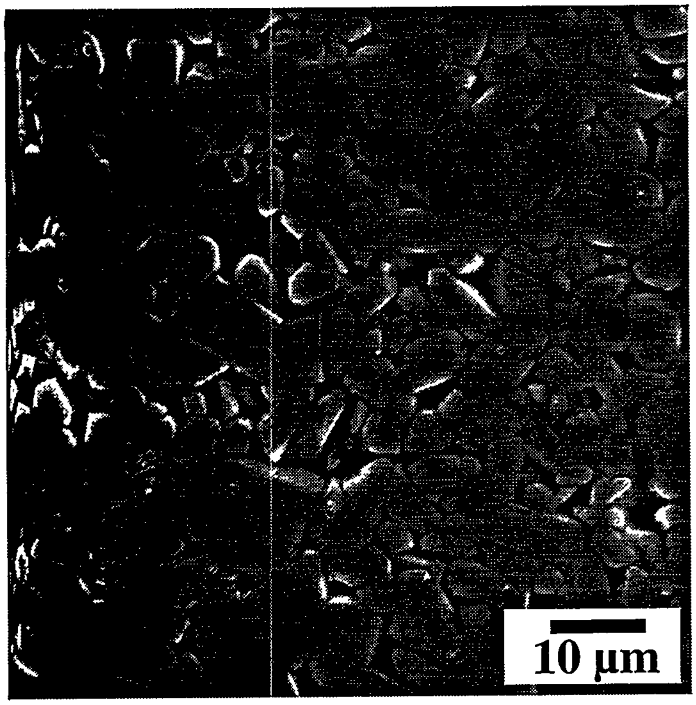


Fig 56

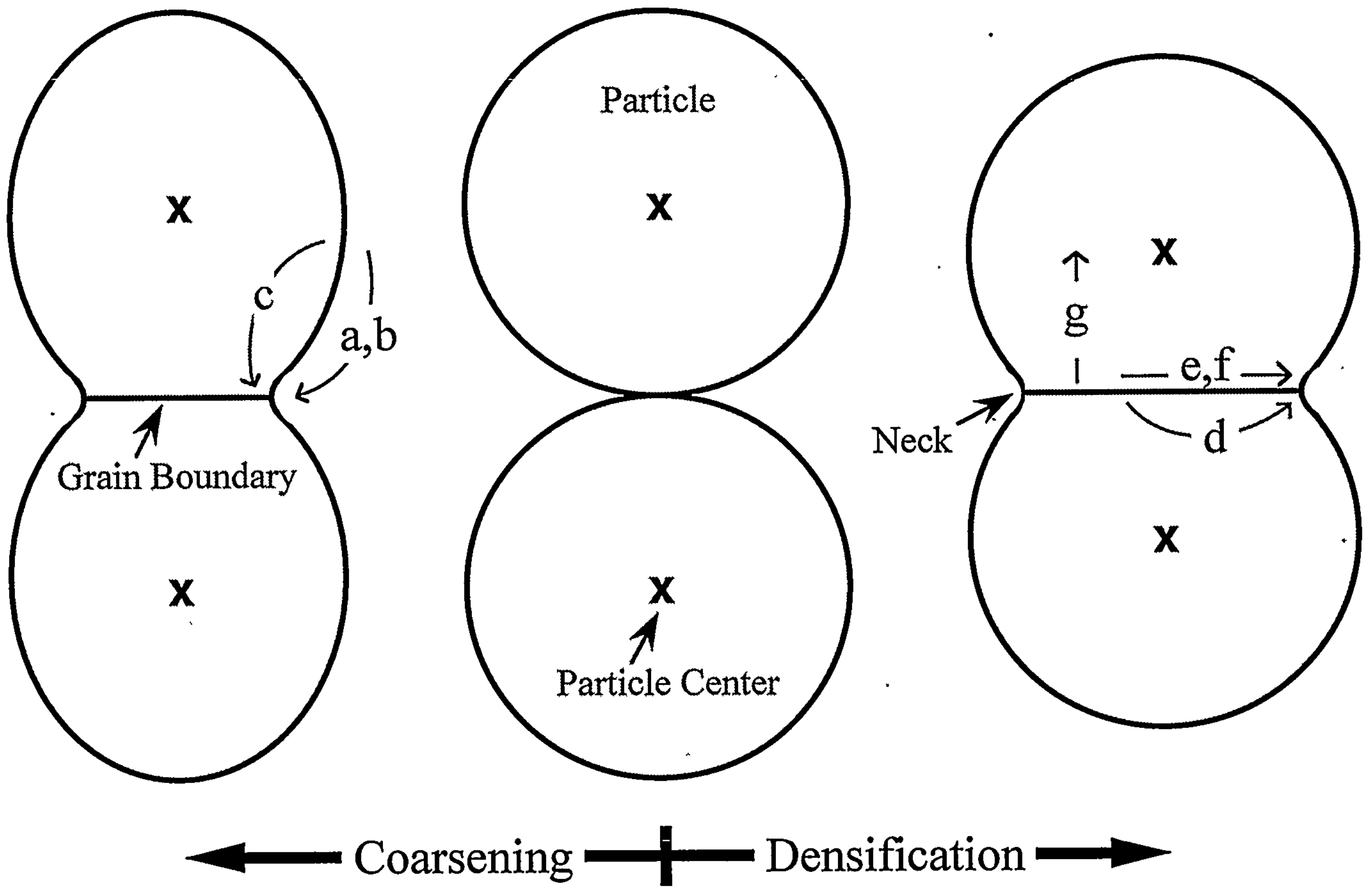

Particle
x
c
a,b
Grain Boundary
Particle Center
Neck
g
e,f
d
Coarsening
Densification

Fig 6

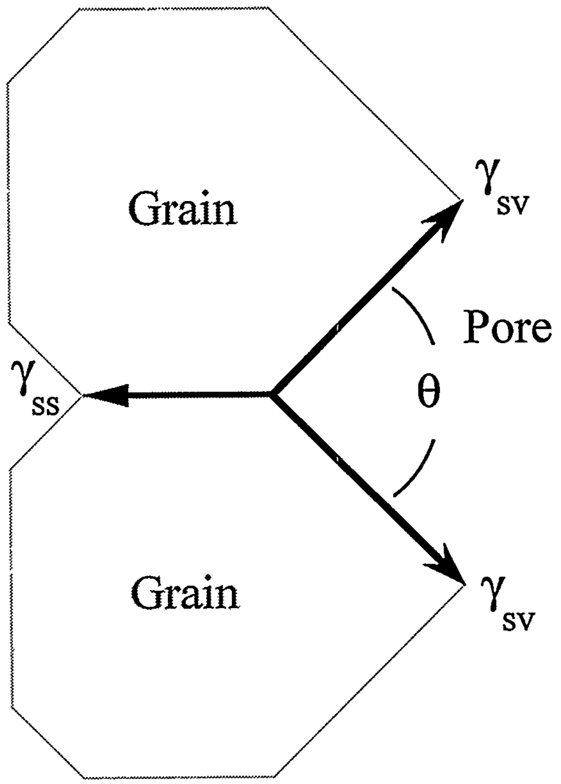


Fig 7

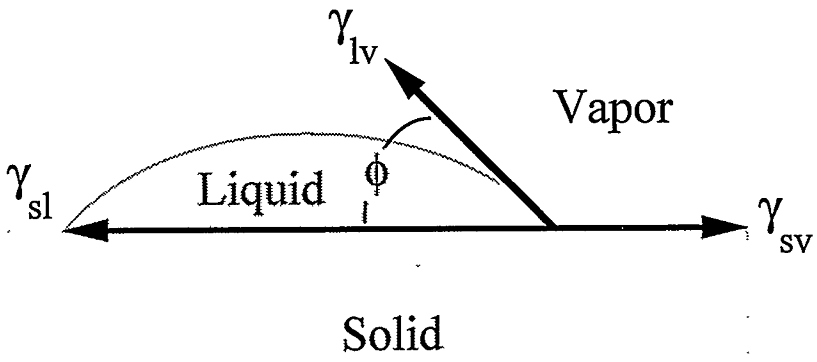


Fig 8