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Development of novel ceramic processing

DIPAK R. BISWAS
Alcatel Cable Systems Group, 7635 Plantation Road, CS # 19000 Roanoke, Virginia 24019, USA

Ceramic materials processing consists of powder preparation and fabrication of components by using these powders. Conventional powder preparation and fabrication of ceramic components along with novel methods are reviewed.

1. Introduction

Ceramic materials are of tremendous interest primarily because of their applications in high temperature environments; they are also extensively used in electronics, glass, insulator, semi and superconductors, and other industries. Ceramic processing is an ancient art and technology, but continuous improvement through research and development makes the process and the product reliable and cost effective. Ceramic processing is mainly divided into two parts: (a) preparation of powders, and (b) fabrication of ceramic components using the powders.

The preparation of powders is normally accomplished by breaking down the large solid mass by crushing, grinding, milling, and screening and by some chemical reactions through phase changes such as vapour–liquid–solid, vapour–solid, vapour–vapour, liquid–solid, and solid–solid. Once the powders are made, their characterization is extremely important as the final microstructure and properties are dependent on initial powder characterization. The characterization of powder includes: chemical and structural, morphology and physical, and bulk properties.

The fabrication of ceramic components generally involves the pressing of powders to the desired shape followed by firing or sintering at relatively high temperatures to obtain high density products.

The purpose of this paper is to review the development of ceramic powder preparation and the fabrication of ceramic components. After an introduction to the conventional methods, novel developments in preparation and fabrication are discussed. These novel techniques can produce pure, fine powders which can produce the desired shaped components with controlled microstructure.

2. Conventional methods of ceramic processing

2.1. Powder preparation

A general flow chart of conventional and novel techniques of ceramic processing is shown in Fig. 1.

The size reduction or breaking down of a large mass such as quartzite, calcite, kaolinite etc. is carried out by crushing and grinding. Sometimes calcination of large particles at 1000 to 1200° C is helpful for ease in breaking down to smaller particles. After crushing with a jaw crusher or crushing roller, the broken particles are further reduced in size by attrition [1] or high impact grinding in a ball mill or rod mill or other types of mills. A screening operation is normally carried out for size separations. The end product of grinding usually produces a combination of relatively coarse and fine particles. It has been found that the powder surface area can be increased by increasing the grinding time [2], but in some cases, the surface area is decreased due to the formation of agglomerates. Contamination [3] of powders during milling is a common problem and normally increases with an increase in milling time, e.g. the activation energy of lead zirconate–titanate (PZT) ceramic is increased from 1.05 to 1.41 eV when PZT powder is milled with zirconia balls compared to alumina balls [4].

Other conventional techniques for powder preparation include (a) spray drying [5, 6] in which a suspension is sprayed from the top of a heated chamber and the dry spherical powders are removed from the bottom, (b) freeze drying [7] which is normally a salt decomposition process where droplets of liquids are rapidly frozen, followed by heating to obtain the final spherical powders, (c) solution precipitation [8] in which a homogeneous solution is mixed with a precipitating agent followed by separating the precipitates by filtering and then decomposing to ceramic powders, e.g. alumina powders by Bayer Process [9]. The control of pH, mixing, and stirring rates are the major parameters. Multicomponent ceramic oxides can also be prepared by coprecipitation, e.g. titanates [10], ferrites [11] and $NiO–Al_2O_3$ [12] powders.

2.2. Fabrication

The conventional ceramic fabrication has been done by dry pressing, isostatic pressing, slip casting, tape casting, extrusion, injection moulding, followed by drying, sintering or hot pressing.

Conventionally, powders with small amount of binders are converted to a wide variety of shapes by uniaxial compaction in dry pressing [13]. Instead of uniaxial pressing, various shapes of ceramic components are fabricated by isostatic pressing in which the powders are loaded in a plastic bag which is then placed in a container and subjected to isostatic pressure, generally 20 000 to 40 000 p.s.i. (1 p.s.i. = 6.895×10^3 Pa). Spark plugs, refractory bricks,

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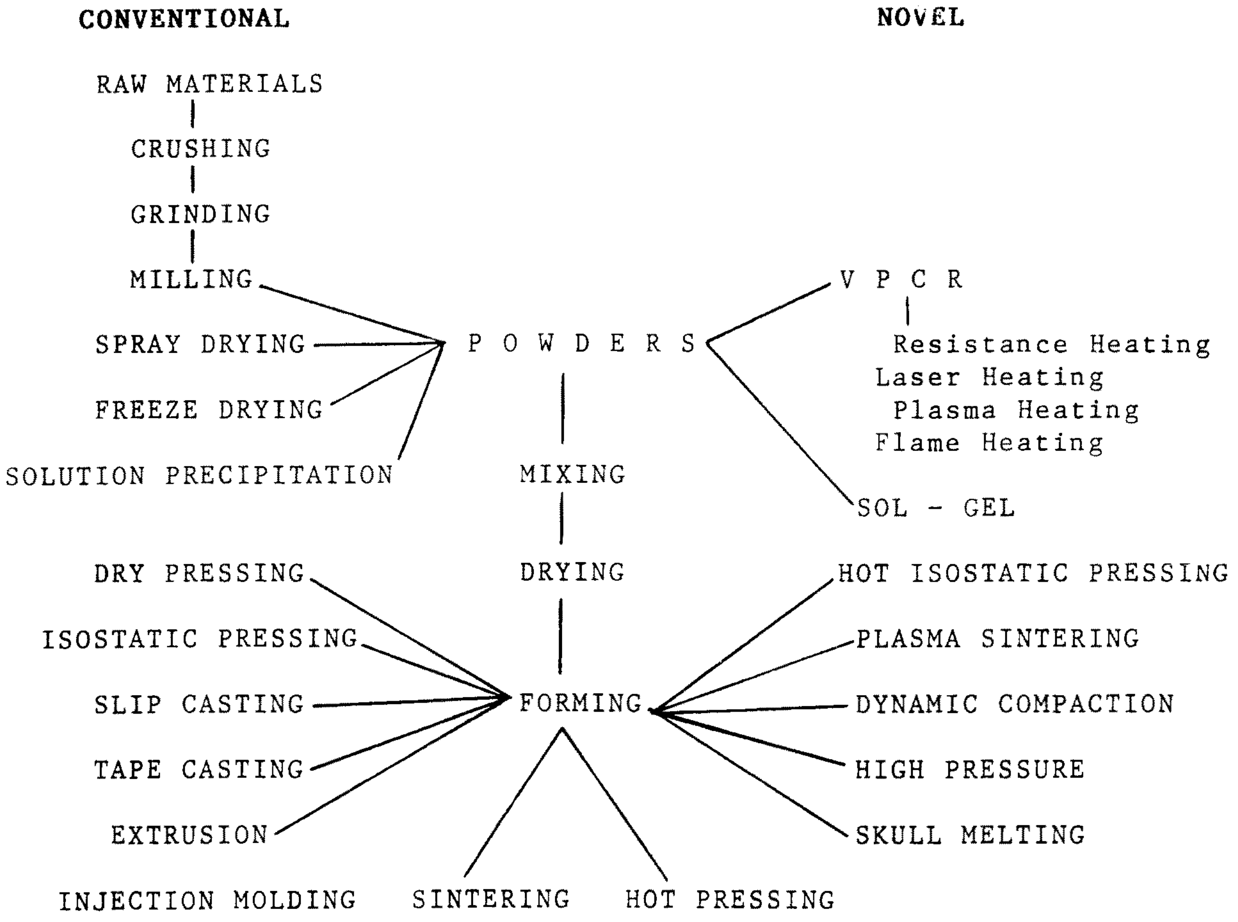

Figure 1 A flow chart of conventional and novel ceramic processing methods.

radomes and carbide tools are just a few examples of ceramics fabricated by isostatic pressing.

Slip casting is an ancient ceramic fabrication process. In this process, powders are suspended in a liquid (normally water) containing dissolved deflocculants and binders to form a slurry. The slurry is then poured into a porous, plaster-of-paris mould where the excess material is removed from the mould cavity producing a finite wall thickness of material. Various ceramic oxides like clays [14], alumina [9], silica [15], magnesia [16], calcia [17], zirconia [18], nitrides [19], fluorides [20], and metallic powders [21, 22] are successfully cast by this process.

Tape casting [23–26] is extensively used in ceramic capacitors, piezoelectrics and insulating substrates for applications in microelectronic circuits. In this process, a ceramic suspension is cast on a smooth surface by using doctor blades for a uniform application and subsequently dried. A thin flexible ceramic tape is then cut into the desired shape and size followed by firing. Other applications of tape casting include the fabrication of electrolyte tubes [27] and fuel cell cathodes [28].

A considerable number of studies have been done on extrusion [29] of clay products. Other ceramic powders, e.g. alumina [30], and β-alumina [31] can also be extruded. The powders, containing different organic additives, are mixed and extruded through a die assembly. The flocculation characteristics and the die design are important parameters.

Injection moulding [32, 33] of ceramic powders is carried out by mixing the powders with a thermoplastic or thermosetting organic carrier with controlled viscosity and injected through a die cavity. Pressure, tool design, injection velocity, and temperature are the major parameters. Complex shapes with precise dimensional control, such as turbine rotor blades can be fabricated by injection moulding [34].

Once the ceramic components have been fabricated by the above mentioned processes, they are fired or sintered at a relatively high temperature for densification. Besides sintering, hot pressing is also used. Hot pressing of ceramic powders is a shaping process in which the pressure is applied to powders in a mould cavity at a high temperature until the powder compact densifies.

3. Novel methods of ceramic processing

3.1. Powder preparation

Fine powders in the submicron range are prepared by using some type of chemical reactions through phase changes [35] such as

(a) Vapour–vapour i.e. one vapour reacts with another vapour in a heat source.

(b) Vapour–liquid–solid i.e. condensation of vapour to liquid followed by solidification.

(c) Vapour–solid i.e. reactions of vapours with solids.

(d) Liquid–solid i.e. crystallization from solution, precipitation and sol–gel.

(e) Solid–solid i.e. decomposition of solid and vapour.

The vapour–vapour reaction, which is called a vapour-phase chemical reaction (VPCR) and the

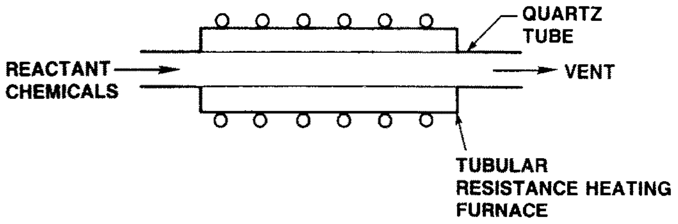

Figure 2 A resistance heating set up for the vapour-phase chemical reaction.

liquid–solid reaction, and the sol–gel process are of considerable interest.

3.1.1. Vapour-phase chemical reaction (VPCR)

In this process, a chemical in vapour form reacts with another vapour at a finite temperature using an available heat source to produce finely divided powders. The overall reaction is

$$A_{(g)} + B_{(g)} = C_{(s)} + D_{(g)}$$

The end solid product can be a film, platelet, whisker or powder. The heat can be supplied by resistance heating, induction heating, laser heating, arcs, plasmas, or flames.

In resistance heating, a simple quartz or alumina tube which is wrapped with a heating element, as shown in Fig. 2, can be used as a heat source. When the gaseous chemicals pass through the hot zone, they react to form powders or films. The film formation inside the tube wall is the major limitation to producing fine powders. Similarly, induction heating is suitable for producing thin films [36, 37] rather than powders.

Laser heating, in contrast, has diverse applications like drilling, welding, glazing, alloying, thin film, and powder processing. Powder processing by VPCR in a laser beam found to be suitable for preparing small, agglomerate free, narrow size ranged, spherical powders. The advantages of using a laser beam [38] as a heat source are its wavelength, narrow spectral width, brightness of emitted light, and contamination free uniform heating. In this process, a mixture of chemical vapours is directly heated by absorbing the laser radiation where the VPCR occurs to produce fine powders as shown in Fig. 3. SiC and Si_3N_4 powders [38] were prepared by reacting silane with methane–ethane, and ammonia in a CO_2 laser beam of fixed wavelength at $10.6\,\mu m$. Silicon powders were also prepared by decomposing silane. The particle size ranged from 0.01 to $0.1\,\mu m$. Laser power intensity, chamber and reactant gas pressure were the major parameters. The final particle size is dependent upon the process of nucleation and growth. The homogeneous nucleation rate, which is the result of instantaneous growth of nuclei, is usually very small. The heterogeneous nucleation rate, which is the result of catalytic action by foreign particles, usually predominates. Once the nuclei exceed the critical size, growth starts at a rate controlled by temperature and degree of supersaturation.

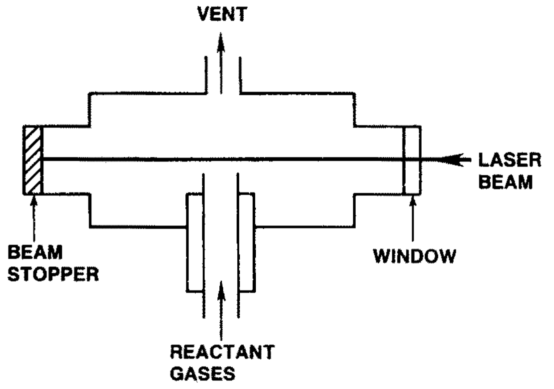

Figure 3 A laser beam heating set up for the vapour-phase chemical reaction.

The growth rate is determined by the provision at which the material transports to surface and the rate at which it can form new bonds in the crystal structure. To produce fine powders, it is necessary to have large numbers of nuclei and to control the growth process by rapid cooling.

For high temperature ceramic powder preparation, the other heat source is a high intensity arc [39–42], in which the graphite is used as both the cathode and anode. The reactant gases are passed through a central bore of the anode and reacted in arc plasma. The plasma is initiated by a high frequency, high voltage spark between the anode and cathode, reaching a temperature as high as 6000–7000° C. The VPCR product, formed out of the tail end of the arc plasma condenses rapidly into very fine powders. High temperature ceramic oxides, and carbides are prepared by this process. Recently extra fine silicon (about 30 nm) powders were produced by the arc plasma [43] method in which a silicon block was placed on a watercooled copper anode and melted by a direct current arc. Ultrafine powders produced was carried away by a mixture of nitrogen and argon gases.

One of the most efficient way of preparing ultrafine ceramic powders of oxides, carbides and nitrides is by using an inductively coupled radio frequency (RF) plasma torch [44–47]. Since there are no electrodes (compared to arc plasma), it can be used in inert, oxidizing, or reducing atmospheres. The torch, as shown in Fig. 4, consists of multiple concentric quartz tubes with independent gas flow lines. The outer tube is surrounded by a RF coil which produces the plasma. The torch is started in an inert gas, normally argon, by coupling the RF coil to a graphite rod inserted into the RF field. The heated tip lowers the breakdown potential and forms plasma which is maintained by increasing the RF energy. Once started, the rod is removed and oxygen, hydrogen, nitrogen or helium is added to argon depending on the type of vapour-phase reactions. In inductively coupled plasma process, the metallic powder and the reactant gas can be fed into the plasma where the metal vapour reacts with the reacting gases to produce the desired powders, such as Al_2O_3–Cr_2O_3 [45] and TiN [47].

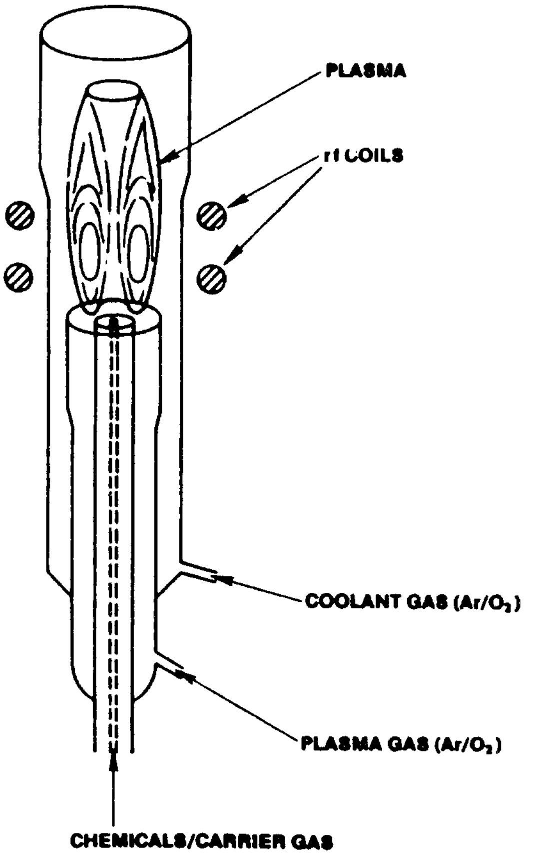

Figure 4 Plasma torch arrangements for the vapour-phase chemical reaction.

Also, the metallic halide with a carrier gas can be fed into the plasma where the oxidation of halides takes place to produce oxides [46, 48]. Similarly carbides [49] can be produced from a mixture of silane, methane and hydrogen is an inductively coupled argon plasma. The very short residence time of the chemical vapours in the plasma reaction zone means that the close control of feed size distribution and feed injection velocity determines [50] the overall efficiency of the process.

Another convenient way to prepare ceramic oxide powders is by using flame torches in which the VPCR takes place inside the flame. The torch generally consists of multiple concentric quartz tubes with independent gas inlets. SiO_2 and GeO_2 powders are prepared by hydrolysis [51, 52] of corresponding halides in an oxy-hydrogen flame as shown in Fig. 5. Using oxy-hydrogen burner [53], silica–germania particles are generated in the production of optical waveguides. Other ceramic oxides like TiO_2 are prepared by oxidation of $TiCl_4$ in a carbon monoxide, oxygen, and nitrogen flame [54]. By changing the flow of gases, the flame shape and size can be varied. By changing the flow of chemicals, usually through the central ring of the torch, the powder characteristics can be altered. The velocity profile at the torch tip can be calculated from the data on individual flow rates and cross-sectional area of its flow channel. Recently [55], it has been found that a saddle-shaped velocity profile at the torch tip allows the deposition rate of oxide particles to go through a maximum when the flow of hydrogen is increased in an oxy-hydrogen flame as shown in Fig. 6. An increase in inner nitrogen flow velocity caused a cooling effect on the deposition process. Interchange of flow channels between hydrogen and oxygen (hydrogen through inner ring) increased the deposition temperature and deposition rate of oxide particles.

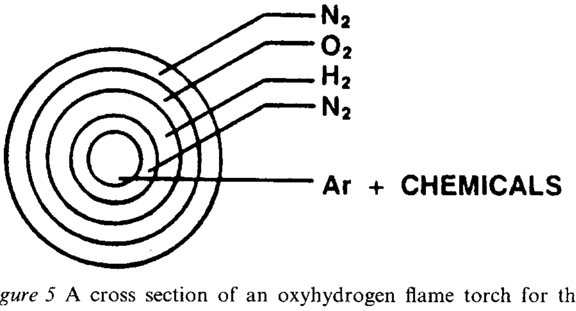

Figure 5 A cross section of an oxyhydrogen flame torch for the vapour-phase chemical reaction [55].

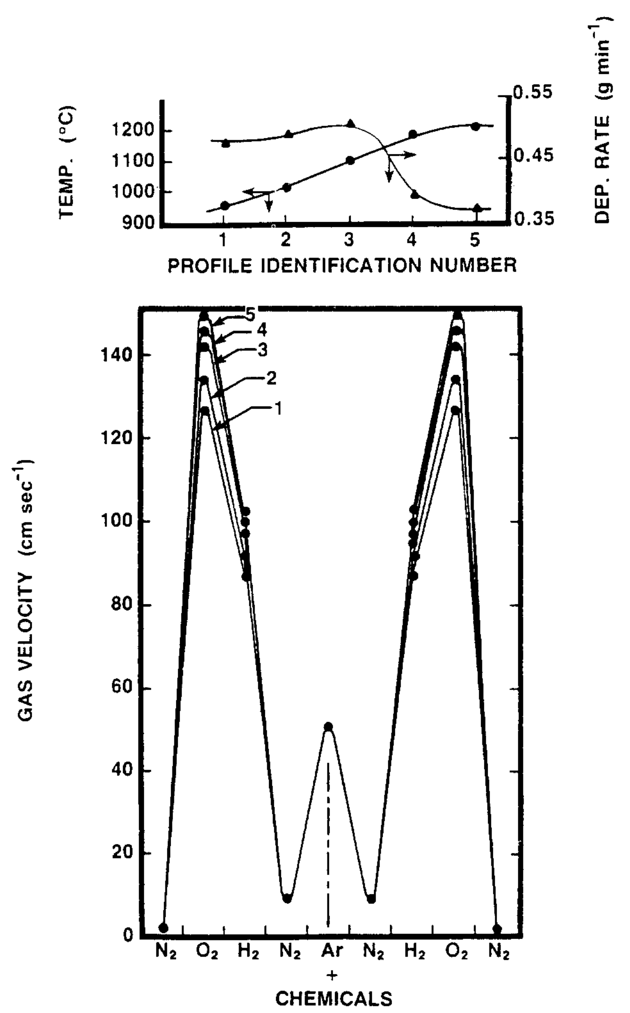

Figure 6 A saddle-shaped velocity profile at the oxyhydrogen torch tip [55].

3.1.2. Sol–gel

The sol–gel process of ceramic powder and glass preparation has received a considerable attention recently [56–61]. The gelling of hydrosols and polymerization of metal alkoxides are the routes to producing powders and ceramic articles by this process. In the gelling process, finely divided powders [61] or metal halides [57] are mixed with water to form gels followed by drying and sintering to obtain ceramic articles. In the polymerization process, metallic alkoxides [58–60] are mixed with water to produce sols which are then polymerized to gels followed by drying and sintering. A considerable amount of work has been done to produce silica gels which are then converted into glasses. Gels produced by hydrolysis of metal alkoxides can be directly nitrided by ammonia to prepare corresponding metal nitride powders such as nitridation [62] of Al_2O_3, $Al(OH)_3$ gels and ammonia to form AlN powders. Recently, TiN fibres are produced by ammonolysis of TiO_2 gel fibres [63]. The major problems associated with this process are the drying cracks that form due to the loss of water, the removal of hydroxyl ions in some special applications and the control of the diameter of rods and length of fibres from the sols.

In the optical fibre industry, the sol–gel method is potentially attractive. Starting with $Si(OEt)_4$ as a precursor, optical fibres with $6\,dB\,km^{-1}$ loss have been made [64].

Other novel processes include the decomposition of salt [66, 67] and gas [68] to produce fine powders. Recently Ando and Uyeda [69] prepared β-silicon carbide powders of less than 0.1 μm diameter by using electrically heated silicon block and carbon rod. Production of large amounts of powders by using this process remained in question. Fine powders of TiN, ZrN, and HfN are prepared by combustion synthesis [70] in which the metallic powder and a solid source of nitrogen (such as sodium azide) is ignited by a tungsten coil. A self propagating reaction front rapidly moves through the reactants completely converting them into nitrides. A solid combustion synthesis of SiC powder is produced by an exothermic reaction of silicon powders with carbon black and charcoal powders at an ignition temperature of 1250 to 1300° C [71]. High temperature reactions in solar furnaces and hydrothermal processing are also used to produce fine powders.

Hydrothermal processing [72] can also produce finely dispersed oxide particles by reacting metallic powders with water under pressure. A new area of ceramic processing in zero gravity is also underway.

3.2. Fabrication

A novel method of achieving nearly 100% theoretical density ceramic components is by hot isostatic pressing (HIP) of powders. Three main areas have evolved during the last thirty years for the production of HIP process parts [73]

(1) Consolidation [74] of powders

(2) Densification of castings and presintered parts, and

(3) Bonding [75] or joining of various components. Hipping for densification to near net shaped parts is of considerable importance. In this process, the powders are pressed into a desired shape either by cold pressing or by isostatic pressing, followed by placing the pressed body in a metallic or glass can and vacuum sealed. It is then hipped at 1000 to 1750° C under 10 000 to 30 000 p.s.i. pressure in an argon or helium atmosphere. After stripping away the can, the near net shaped parts can be released. Carbides and nitrides are routinely fabricated by the hipping process. Silicon nitride powders are hipped [76] to 94% of theoretical density without any additives. The high density, uniform microstructure, low grain growth and occasional flaw healing by hipping makes the process effective. The can design and the sample handling are the critical factors.

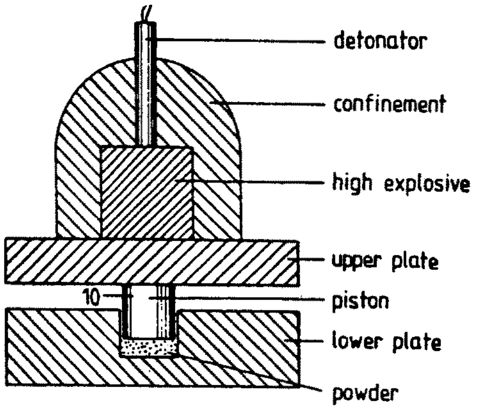

Figure 7 A direct method of explosive compaction of powders [85].

Near-net-shaped ceramics can also be made by sinter-forging [77] in which the blanks are made by cold isostatic pressing and then hot forged between graphite dies.

Ultrarapid densification of ceramic components like rods, and tubes can be achieved in plasma generated microwave cavity [78–80]. Higher density, small grain size, and improved mechanical strength of ceramic components are achieved by this process. An inductively coupled plasma was generated inside a quartz tube surrounded by an outer jacket of borosilicate glass tube by using an RF generator. Densities greater than 98% of the theoretical value were obtained in less than 90 sec in the case of β-alumina tubes [78]. Besides inductively coupled plasmas, a glow discharge [81, 82] in a cylindrical hollow cathode was used to sinter alumina rods and UO_2 pellets to achieve densities as high as 99% of the theoretical value. The thickness and the feed rate of samples in plasma are critical from the point of view of thermal shock and complete densification in high temperature plasma.

Dynamic compaction techniques are suitable for consolidation of rapidly solidified and thermally unstable powders [83–85]. A high pressure shock which is generated by the impact of a fast moving projectile, passes through the powder and compaction takes place. Surface deformation and heating due to friction occurs during compaction. Also there is some localized melting [84] which is responsible for particle-to-particle bonding during this process. A direct method of explosive compaction [85], of powders is shown in Fig. 7. The detonation starts at the upper end of the chamber and the shock wave propagates downward in an axial direction which compacts the powder. During the shock, the pressure normally exceeds the shear strength of powder material by a large extent while the heat generated due to friction among particles causes localized melting. When the molten material rapidly cools, it produces amorphous material. Crystallographic changes from layered rhombohedral boron nitride to cubic boron nitride was carried out by explosive shock compression [86]. For small cylindrical samples [87] near theoretical densities can be obtained for different ceramic materials such as Al_2O_3, B_4C. For larger samples, macro and microcracking [88] occurs in explosively compacted materials. This is the major limitation of this process for commercial production at this time. Another ceramic fabrication technique is the use of high pressure [89] during sintering [90] or hot pressing [91]. By using nitrogen pressure [92] of 150 p.s.i. at 1900° C, silicon nitride was pressed to 95% of the theoretical density. Silicon nitride powders were also sintered at 1800 to 1950° C under nitrogen pressures [93] of 250 to 3000 p.s.i. with minimal degradation of material. Other materials like SiC, B_4C, BN and diamond are prepared by high pressure sintering of powders.

A relatively new method of fabricating refractory crystals from the melt growth of ceramic powders, like zirconia and β-alumina by skull melting [94–97] in a cold crucible is found to be most suitable. In this process [96], a cup-like arrangement made by a circle of copper fingers surrounded by a water cooled RF coil, usually operates at 3 to 5 MHz frequency and at power levels as high as 100 kW. In case of cubic zirconia, the zirconia and yttria powders with some zirconia metal pieces as conductors, are loaded into the cup and heated rapidly by RF energy. The zirconia metal pieces heat up quickly and start conducting electrically and melts the powders in a matter of minutes. All the powders melt except for a thin layer which is adjacent to the water cooled cup fingers. Molten zirconia is contained within the sintered zirconia skull, with a porous crust at the top of the melt and equilibriate as shown in Fig. 8. The cup is then lowered very slowly from the heating coil and crystal growth begins at the bottom of the melt as shown in Fig. 8b, and continues to grow until the whole melt solidifies as shown in Fig. 8c. Commercial production of cubic zirconia has already started. A typical batch containing 150 lbs (68 kg) of powders in a 12 inch (30.48 cm) skull yields about 100 lbs (45.3 kg) of crystals.

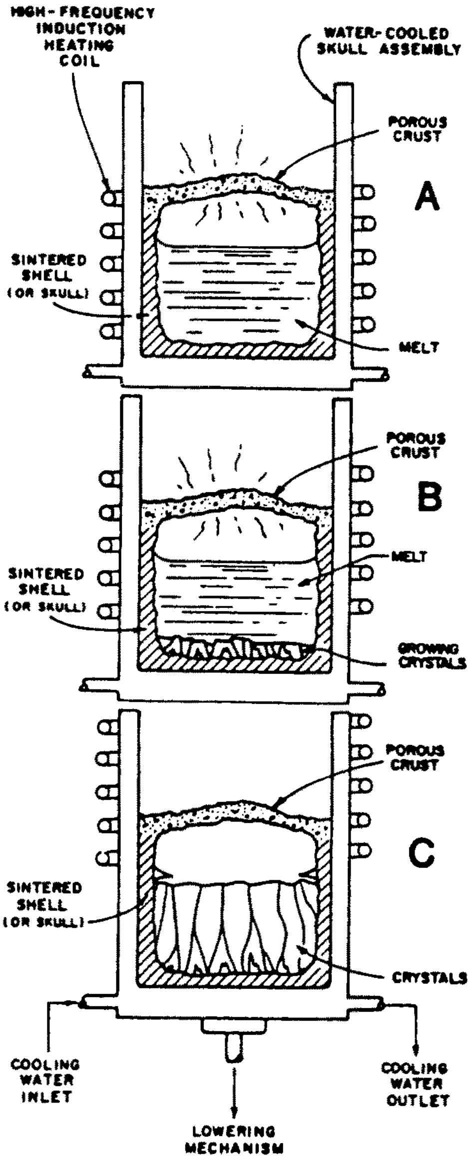

Figure 8 Skull melting crystal growth process. (a) Formation of a porous crust over top of the melt. (b) Early growth of crystals. (c) Final growth of crystals [96].

4. Summary and conclusion

High temperature ceramic material processing mainly consists of the preparation of powders and fabrication of parts using those powders. The conventional methods of powder preparation includes crushing, grinding and screening, spray drying, freeze drying, and solution-precipitation. Fine powders in submicrometre sizes are made by novel methods using some types of chemical reactions through phase changes. Vapour-phase chemical reaction and sol–gel methods producing fine powders are suitable for making high temperature ceramic components with controlled microstructure. In vapour-phase chemical reactions, vapours are reacted or thermally decomposed at a finite temperature to produce fine powders. The heat sources suitable for novel powder preparation are laser heating, plasma heating, and flame torches. Virtually any ceramic oxide, carbide, nitride powders can be made by this process. The sol–gel process in which gelling of hydrosols, and chemical polymerization of metal alkoxides are novel ways to produce ceramic powders and glasses. These powders are conventionally dry pressed, isostatically pressed, slip casted, tape casted, extruded, and injection moulded and then sintered or hot pressed. The novel methods of fabricating the ceramic components are hot isostatic pressing, ultra pressing, ultra rapid densification in inductively coupled plasma, dynamic compaction of powders by using a high pressure shock wave, and skull melting by RF induction. These novel methods of powder preparation and fabrication techniques are beginning to depart from the conventional ceramic processing for reasons of mass production of high purity, well controlled microstructure, and reproducible high temperature ceramic components.

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