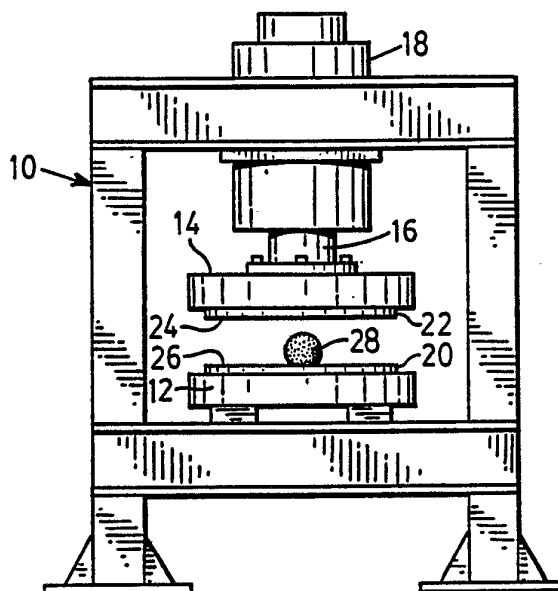




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(54) Title: METHOD OF MANUFACTURING ARTICLES FROM POWDERED MATERIALS**(57) Abstract**

Pasty materials from which green parts are molded before sintering, and which otherwise are difficult or impossible to mix while in the pasty state, are mixed and homogenised by forming a lump, placing it between two parallel flat platens, and pressing the platens together until the lump becomes a thin flat pancake; thereafter the pancake is remade into a lump or ball by moving its circumferential edges inwards. This press-mixing cycle is repeated until the process is sufficiently complete, typically involving from 10 to 50 repetitions, usually about 20 to 30. Molded ceramic articles with "mirror-finish" surfaces are produced economically by employment of small amounts, 5 % or less, of superplastic shear deformation produced by molding the articles with the surfaces to be finished in contact with mold surfaces of the required finish. The starting powdered ceramic materials are of particle size one micrometer or less, and molded green parts are formed using slurring, grinding, and mixing techniques that maintain material uniformity and keep the particle size below one micrometer. The green parts sintered using rate controlled sintering to maintain grain size below the one micrometer value critical for superplastic forging. The sintered parts are then molded as described at a temperature above the minimum superplastic temperature of 0.5 M, where M is the melting temperature of the ceramic material.

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METHOD OF MANUFACTURING ARTICLES FROM POWDERED MATERIALSTECHNICAL FIELD

5 The present invention is concerned with new methods for the mixing and/or homogenisation of powdered materials when this is a step of a manufacturing method for producing an article thereof. The invention is also concerned with new methods of manufacturing articles from powdered materials and especially,
10 but not exclusively, with new methods of producing from powdered ceramic materials thin flat plates which have at least one surface of high surface finish.

BACKGROUND ART

15 Manufacturing processes starting from sintered powdered ceramic and metal materials, involve the production of so-called "green" ware or bodies from finely divided bulk material, or mixtures of materials, which subsequently are heated to a sintering temperature to form the finished products. It is
20 important for satisfactory production that the initial processing produce a material to be heated that is as uniform as possible in its constitution, and that is as free as possible from physical and chemical flaws and inhomogenities (referred to herein generically as "flaws"), since these determine many
25 critical properties of the final products. It is known for example that with ceramic products any such flaws present in the green ware are amplified during the firing, and subsequent fractures in the finished products are almost always initiated at the regions containing such flaws. The flaws also have
30 deleterious effects on properties such as thermal shock resistance, dielectric strength and high temperature deformation, and for ceramic products intended for high strength applications flaws as small as 10 micrometres may still be too large. Because of the difficulty with existing preparation
35 methods of avoiding small dimension flaws ceramic parts for high strength applications may require proof testing of every part, considerably increasing their cost.

The methods usually employed hitherto for the

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production of sintered ceramics or metal parts basically involve stirring together predetermined amounts of binders, surfactants and functional agents in water, or other suitable aqueous or non-aqueous solvents, until they are completely dissolved.

5 During or after this mixing step the powdered base material is added to the solution while stirring continuously until it is fully dispersed and deagglomerated, the stirring usually being carried out in high shear mixing apparatus such as ball mills, or vessels employing rotating stirring devices, etc. The
10 resulting slurry is referred to in the ceramic industry as "slip". The continued stirring (aging) of the slip after the addition of all of the ingredients may require anywhere from two hours to four days, depending upon the equipment available and the end-quality of slip that is required. The slip is then
15 dried, the three principal methods used being spray-drying, filter-pressing or tape-casting, to achieve a more-or-less dry appearing material containing anywhere from 1% up to 40% by weight of moisture, this material then being molded or punched to form the "green" parts that subsequently are sintered, the
20 sintering firing removing residual moisture, binders, and functional agents. Ideally the resultant product, whether of polycrystalline ceramic or metal, remains completely homogeneous and is pore and residue free with no impurities that were introduced during the mixing and drying steps.

25 It has been realised that the successful production of ceramic and powdered metal parts required careful control of the particle size of the starting material, careful control of the grain or crystallite size of the sintered material, and in addition, careful control of the range of particle and grain
30 sizes that are present. One of the purposes of the relatively lengthy ageing step is to ensure that the particles of different sizes and density are distributed as uniformly as possible throughout the material, and all of the drying methods mentioned have the problem that inherently they reintroduce non-uniformity
35 in the dried material.

In spray-drying the slip is pumped through a nozzle to form a spray which is dewatered by heat and reduced pressure. The spray is of random droplet size, some of which droplets will

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be able to contain only small size particles, and some of which particles will be hollow, resulting in a relatively low density, while other droplets will contain single solid large particles, resulting in higher densities. The droplets of different sizes and densities, and the particles of different sizes and densities as they are released from the droplets, will fall at different rates and in different locations resulting in an undesired partial classification. Also due to the different particle sizes and densities some additional separation may occur during the subsequent bulk handling of the particles.

When a slurry is press-filtered the exiting moisture must pass out through the remainder of the body to reach the surface of the body and it tends to carry the finer particles with it while leaving the larger particles behind, so that the dewatered material is partially segregated with an excess of finer particles in its outer portion, and an excess of larger particles in its centre.

In tape casting the slurry is deposited on a moving conveyor in the form of a thin film or strip that is passed through a drying chamber, the resulting dried strip upon removal is usually self-supporting to the extent that it can be rolled for storage and subsequent processing and again partial segregation and non-uniformities are obtained.

The electronics industry is an example of one which now makes substantial use of so-called thin film substrates, which are thin flat pieces of sintered ceramic material produced to very high quality specifications as to starting material and physical characteristics. For example, such substrates that are used for hybrid electronic circuit applications often take the form of square plates of 5cm (2ins.) side and 0.38mm (0.015in.) thickness, and usually are made from alumina, aluminum nitride, zirconia or beryllia. They are required to have highly uniform values of thickness, grain size, grain structure, density, surface flatness and surface finish, with the purpose of obtaining uniform dielectric constant and sheet resistivity, and also to permit the production on the surfaces of fine uniform width and uniformly spaced conducting lines that provide minimum signal losses and uniform impedances. As a specific example,

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such substrates are manufactured from alumina to have an alumina content of 99.5%-99.6%, an average grain size of 1.2-2.2 micrometers, and a bulk density of 3.8-3.9. They must have as a minimum a surface finish of less than 0.012 micrometers (0.5 microinch) with an absence of abrasive damage, a flatness tolerance of 1.2 micrometers per cm (0.0005 in. per in.), and a thickness tolerance of ± 12 micrometers (± 0.0005 in.); finer tolerances than these are often required. The production of plates to these high standards requires costly surface finishing by diamond grinding and polishing owing to the intrinsic difficulty hitherto of obtaining sufficiently smooth and uniform surfaces with sintered ceramics, and consequently is expensive with a relatively high rejection rate.

15 DISCLOSURE OF INVENTION

It is the principal object of the invention to provide a new method of mixing and/or homogenising partly dried pasty materials prior to a firing step in order to obtain uniformity of particle distribution.

20 It is another principal object to provide a new method of manufacturing ceramic articles with excellent finish surface characteristics without the need for surface grinding.

In accordance with the present invention there is provided a method for the mixing and/or homogenisation of pasty material comprising the steps of:

- a) placing a mass of the pasty material in the form of a lump between two relatively movable press members having opposed respective parallel press surfaces;
- b) moving the press members linearly toward one another under pressure so that the press surfaces engage the pasty material and continuing the movement until the lump is flattened to a thin pancake-like form;
- c) moving the press members away from one another to permit access to the resultant thin pancake;
- d) accessing the pancake and returning the pasty material to the form of a lump by inward rolling movement of the pancake periphery toward its centre; and
- e) repeating steps a)-d) until the desired amount of

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mixing and/or homogenisation has been obtained.

Also in accordance with the invention there is provided a method of manufacturing molded articles from powdered materials including the steps of:

preparing a sintered body of the powdered material with grain size 1 micrometer or less so as to permit superplastic forging thereof;

depositing the sintered body in a mold having at least one finished mold surface of the surface finish required for a corresponding surface to be finished of the molded article, the body in the mold being heated to a superplastic forging temperature of at least $0.5M$ where M is the melting temperature of the material; and

while the sintered body in the mold is at the said forging temperature applying pressure thereto of a value, for a time, and in a direction such as to produce superplastic forging and molding of at least the said body surface to be finished in contact with the said finished mold surface so as to impart the same surface finish to the body surface to be finished;

the superplastic forging and molding being carried out to obtain a shear deformation of the sintered body of not more than 5%.

Preferably the superplastic forging and molding is carried out to obtain a superplastic shear deformation of the sintered body of between 1% and 3%, and preferably the sintered body is sintered to at least 99.5% of theoretical density. Preferably also the sintered body is prepared using the method for the mixing and/or homogenisation of pasty material specified above.

DESCRIPTION OF THE DRAWINGS

Methods and apparatus that are particular preferred embodiments of the invention will now be described, by way of example, with reference to the accompanying diagrammatic drawings wherein:-

Figure 1 is a front elevation of a hydraulic press employed in the performance of a mixing and/or homogenisation

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method constituting a step of an article manufacturing method;

Figure 2 is a top perspective view illustrating a first major step of the mixing and/or homogenisation method;

Figure 3 is a similar view to Figure 2 illustrating a
5 second major step of the mixing and/or homogenisation method;

Figure 4 is a similar view to Figures 2 and 3 illustrating a third major step of the mixing and/or homogenisation method, which is followed by the first major step for the sequence to repeat as many times as required;

10 Figure 5 is a perspective view of another hydraulic press for the mixing and/or homogenisation method employing mechanical vibration to augment the pressing step;

Figure 6 is a side elevation of a reverbatory ultrasonic mixer used in the performance of another step of an
15 article manufacturing method;

Figure 7 is a part end elevation and part transverse cross-section through a hot press that is used to perform a further step of an article manufacturing method;

Figure 8 is a top perspective view to an enlarged scale
20 of mold top and bottom plates used with the press of Figure 7;

Figure 9 is a cross-section through part of the mold top and bottom plates with the mold open, with a sintered ceramic part placed therein at room temperature shown in broken lines, and with the ceramic part at superplastic forging
25 temperature shown in solid lines;

Figure 10 is a view similar to Figure 9 with the mold closed and the superplastic forging and surface finishing step completed; and

Figure 11 is a top perspective view similar to Figure 8
30 of another mold for use with the press of Figure 7.

MODES FOR CARRYING OUT THE INVENTION

The methods of the invention are applicable to the "advanced" ceramic materials that are now used in industry, the
35 most common of which are alumina, zirconia, silicon nitride and aluminum nitride. Of these the most commonly used at this time is alumina, and the invention will be described as applied to the production of substrates for electronics applications

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produced by sintering bodies of this material. Such substrates are usually produced as squares or rectangles of side length between 5cm (2in.) and 11.25cm (4.5in.) and thickness between 0.125mm (0.005in) and 1mm (0.040in.). A typical industrial specification for such a substrate will include required values for a large number of physical properties including alumina content, color, bulk density (range), hardness (Rockwell), surface finish, grain size (average), water absorption (%), flexural strength, modulus of elasticity, poisson's ratio, coefficient of linear thermal expansion, thermal conductivity, dielectric strength, dielectric constant, dissipation factor, loss index, and volume resistivity. Of these many factors one of the most important is the surface finish to permit fine line widths and fine spacing of the conductors that are deposited on the surface, and the achievement of the high quality finish prescribed, usually less than 0.125 micrometres (5 microins) and frequently less than 0.075 micrometres (3 microins), is difficult to achieve with ceramic materials because of their inherent hardness and very irregular surface as produced by sintering. As described above, hitherto the required highly smooth (mirror finish) surfaces have been produced by relatively expensive grinding and polishing operations on the sintered plates, with the high possibility of low yields owing for example to abrasive damage inadvertently produced by the grinding and polishing operations.

A first step in the processes of the invention is to form a slurry using powdered material of one micrometer particle size or less, this maximum particle size being a requirement for superplastic forging of ceramic materials, as is disclosed for example at pages 253-255 of the publication "Forming, Shaping and Working of High-Performance Ceramics", by I. J. McCollm and N. J. Clark, published in 1988 by Blackie & Son Ltd., Glasgow, Scotland. The slurry may be aqueous or non-aqueous, although aqueous slurries are usually preferred; an aqueous slurry will include a binder such as methyl cellulose in the amount of 0.8%-1.5% by weight, and a surfactant such as DARVAN (Trade Mark) in the amount of 0.1%-1% by weight. Other functional agents may also be included. The powdered alumina, binder and

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surfactant are added progressively to the suspending liquid until the solids content is in the range of 25%-60% by weight. The methods of production of such slurries, whether aqueous or non-aqueous, are well known to those skilled in the production
5 of sintered ceramic materials and need not be further described.

The formation of the slurry usually results in agglomeration of many of the fine particles, so that they are no longer all of one micrometer size or less, and this must be corrected, as described above, by stirring and/or grinding the
10 slurry using any of the apparatus conventionally used for this purpose, such as ball or rod mills and high shear stirrers. Typically with the processes of the invention when the deagglomerating apparatus is a ball-mill this will require operation for a period of from about 12 to 72 hours.

15 Although at the end of this step the deagglomerating apparatus will have produced sufficient physical uniformity of the slurry, it may not necessarily have produced chemical uniformity with the surfacant distributed uniformly over the finely powdered alumina, and one way of improving this chemical
20 uniformity is to subject the slurry to the effect of intense ultrasonic energy, preferably in a reverbatory ultrasonic mixing (R.U.M.) apparatus as illustrated by Figure 6, and as described in more detail in my U.S. Patent Serial No. 4,071,225, the disclosure of which is incorporated herein by this reference.
25 The effect of the R.U.M. apparatus is also to deagglomerate and produce physical uniformity to the extent that in some processes the prior stirring and/or grinding operation may not be needed.

Referring to Figure 6 herein, the R.U.M. apparatus includes a storage container 36 into which the slurry is loaded,
30 the container being provided with a mixing paddle 38 driven by a motor 40. A pipe 42 feeds the slurry to a pressure pump 44, and a pipe 46 feeds the pressurized slurry to the interior of an ultrasonic cell 48. Another pipe 50 feeds the slurry that exits from the cell through a valve 52 and hence back to the container
35 interior, so that the container contents can be recirculated until the dispersion has proceeded to the required extent. An outlet valve 54 is also provided.

The cell 48 consists of a metal frame 56 providing a

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chamber between two flat closely-spaced (i.e. usually less than 6mm) metal plates that is of thin highly-elongated, rectangular cross-section. Pressure gauges 58 are provided to monitor the inlet and outlet pressures. The two wide, closely-spaced, parallel, oscillation applying walls of the cell are constituted by respective thin sheet metal membranes fastened at their edges to the frame 56, each of the walls having a large plurality of ultrasonic transducers 46 mounted thereon, the transducers directing the longitudinal pressure waves they generate into the pressurized liquid in the enclosure perpendicularly to the plane of the walls and also to the direction of flow. The transducers are connected to a suitable source of power which is not illustrated. A batch of the ceramic slurry will require processing for a period of about 20-30 minutes to achieve the desired chemical uniformity.

The thoroughly dispersed slurry obtained from this apparatus is now dewatered, for example in a filter press, until a solids content of at least 70%-90% by weight is obtained. As has been described above, such dewatering produces undesirable classification and physical non-uniformity of the resultant pasty material and physical uniformity preferably is restored by the employment of a press-mixing operation of the invention, illustrated by Figures 2 through 4, using an apparatus as illustrated by Figure 1 or 5, and described in detail below.

The press-mixing operation results in either a ball or a thin pancake of uniformly dispersed sub-micrometer pasty material, which conveniently is now sub-divided into smaller portions of the shape required for the final high-surface finish articles. Thus, if the pancake can be made sufficiently thin then it can be cut directly into plates of the required size and shape. If this is not possible then the ball or pancake is cut into portions which preferably are transfer molded to be of the required size and shape. Injection molding is to be avoided, since it tends to again destroy the uniformity of the product, and there is in addition a high possibility of causing inclusion of impurities consisting of minute particles of metal abraded from the screw and nozzle by the highly abrasive pasty material as it moves through the apparatus. In transfer molding the slug

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of pasty material that is placed in the molding cylinder is slightly larger than the cavity, and the piston is provided with a bleed passage through which the excess material can escape from the cavity when the mold is fully closed; there is
5 therefore a minimum of movement of the material in the cavity relative to the surfaces of the mold cylinder and piston, so that non-uniformity and abrasive particle inclusion is minimized.

Another acceptable procedure for producing the green bodies is extrusion using a cylinder and piston to provide the
10 extrusion pressure, a rod produced by the extrusion is cut into slugs of the required length for later transfer molding as it emerges; the surfaces of such apparatus that contact the pasty material can be hardened to reduce abrasion and such apparatus involves minimal relative movement between the material and
15 these surfaces.

The resultant green articles are now sintered using a sintering process that will ensure that all of the grains or crystallites of the sintered article will not grow, or if they do grow will still remain at a size of one micrometer or less.
20 Such processes are for example those described by Hayne Palmour III et al in a paper entitled "Rate Controlled Sintering Revisited", or as described in Chapter 24, Pages 307-320 of the textbook "Ceramic Processing before Firing", published 1978 by John Wiley and Sons, the authors of this chapter being Hayne
25 Palmour III and T.M. Hare.

Various processes employing sintered materials require different degrees of sintering at different stages of the processes. For example, the material may be only partly sintered in the absence of pressure, the remainder of the
30 sintering being carried out under pressure to remove porosity and obtain as uniform a density as possible. The principal purpose of the processes of the present invention is to obtain superior surface finishes in an economical manner, and for this purpose it is preferred to use fully sintered materials in the
35 superplastic forging and molding operation. Full sintering to 100% of theoretical density is not absolutely necessary for successful operation although values of 99.5% or better are preferred; with values that are lower than this open pores may

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begin to appear in the finished product and if these are not unacceptable then lower levels down to about 95% of theoretical density may perhaps be tolerated.

The sintered ceramic articles that are thus produced
5 are found usually to have a surface finish such that the vertical distances between peaks and valleys is in the range 1 to 80 micrometers, and can be as much as 120 micrometers, and therefore they cannot be used as substrates without further processing, which as described above, previously consisted of
10 diamond grinding and polishing. The statistical reliability, or relative absence of catastrophic failure, of ceramic products commonly is characterised by the so-called "Weibull" number, a low value of which is about 2, an average value in the range 5-10, a good value 15 and an exceptional value in the range
15 20-25. The micro-cracks and micro-scratches that are produced by the typical diamond grinding and polishing reduces the Weibull number to the low and average ranges.

A press apparatus for the final superplastic forging and molding step is illustrated by Figures 7 through 11,
20 comprising a frame 62 supporting a cylinder 64 of a hydraulic motor. An enclosure 66 having a sealable, openable door (not shown) is mounted in the frame on a support part 68, which also supports at its upper end a lower mold back-up plate 70. A piston 72 of the hydraulic motor passes through the enclosure
25 wall and carries at its lower end an upper mold back-up plate 74. The interior of the enclosure can be evacuated, or can be supplied with various gases as required by means which will be known to those skilled in this art, and which need not be illustrated. The lower and upper back-up plates carry
30 respective heat insulating plates 76, each of which in turn carries a respective heater element 78 connected to a controllable power supply (not shown). The lower heater element carries a metal lower mold plate 80, and the upper heater element carries a metal upper mold plate 82, the mold
35 plates being shown to an enlarged scale in Figures 8-11.

The lower mold plate 80 has therein, opening to its flat upper butting face 83, a plurality of recesses 84, which in this embodiment are square in plan, in each of which a

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respective thin flat square plate piece 86 will be formed. The flat bottom surfaces 88 of the recesses and the flat undersurface 90 of the upper mold plate are finished to the surface finish that is required for the corresponding butting surfaces of the pieces 86, and usually this will be in the range 0.01-0.005 micrometers (0.5-2 microins). The finish and flatness that can be obtained will of course depend upon the metal from which the mold plates are made, the techniques employed to produce the flat surfaces and, since increased finish and flatness usually involves correspondingly increased costs, what level of finish and flatness is economic and cost effective for the particular article that is to be manufactured. The already sintered pre-formed pieces are deposited in the recesses and are slightly smaller than their cavities when inserted, as indicated in broken lines in Figure 9, so that they can easily be placed therein. The metal from which at least the lower mold plate is made has a lower coefficient of thermal expansion than the ceramic material, and the latter will therefore expand more as it is heated, the cavities 84 being designed to be at their required dimensions at the operating superplastic temperature. The cavities are also dimensioned such that their volume when the mold plates are fully closed together is less than the volume of the sintered body at the superplastic temperature by the small amount of shear displacement reduction that will be produced by the superplastic forging, i.e. not more than 5% by volume, and usually between 2% and 3% by volume.

One requirement for successful superplastic forging is that it is carried out at a temperature which is at least 0.5 of the melting temperature of the material. The melting temperature of alumina is 2072°C, so that the minimum temperature required is about 1000°C; in practice a higher temperature of about 1250°C is preferred. The precise temperature to be employed will depend upon a number of considerations. As high a temperature as possible facilitates the forging since the ceramic material is softer, but is offset by the possibility of causing grain or crystallite growth in the sintered material to above the one micrometer limit, especially

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in the outer border portions of the ceramic plates, so that a compromise is necessary. Another adverse possibility of too high a temperature is the recrystallisation of the metal of the mold plates with consequent loss of surface finish. The preferred mode of operation is for the loaded mold to be placed in the press with the mold plates slightly apart, the mold plates and the contained sintered pieces being heated using the press heating elements 78 until they are at least at the minimum superplastic temperature, and preferably above that minimum temperature, although they need not be at the final maximum temperature, before the two mold plates are closed together under the pressure of the hydraulic motor.

As described above, if the surfaces of the sintered pieces are examined microscopically, they are found to be relatively rough with well-defined peaks and valleys. As the mold is slowly closed it is the peaks that first engage the highly finished mold surfaces and the effective pressure per square cm on these peaks is extremely high, to the extent that superplastic flow will begin. As the peaks are squeezed downward and greater surface areas are engaged the force applied will still be sufficient for superplastic flow, and this will continue progressively predominantly at the two surfaces of the ceramic plates perpendicular to the pressing force, then into the portions of the ceramic plates bordering these surfaces. The shear deformations obtained with the small amounts of superplastic forging characteristic of the invention are by operation of the process predominantly at the butting surfaces at right angles to the pressing force, although the faces parallel to the force will also be molded against their respective mold walls, and all of these butting surfaces will be molded to the surface finish of their mold faces. The selection of the proper refractory metal for the mold will ensure that the ceramic pieces will not stick to the metal walls upon cooling of the mold, so that the molded pieces can be removed without difficulty. The molded plates 86 are now found to have mirror finish surfaces that do not require grinding, and that require at most a minor final polish operation, with the possibility of obtaining Weibull numbers of 25 or better.

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The sintered pieces should be at a temperature above the minimum superplastic temperature before the mold is closed to ensure that the material is sufficiently soft that their relatively rough surfaces will not damage the superior surface finish of the mold faces by penetration. The mold can however be closed if the sintered pieces are sufficiently smaller than the mold cavity that such deleterious contact does not occur before the superplastic temperature is reached; the final portion of the temperature rise to maximum operating temperature is now obtained while the mold is closed, and this will with this version of the method be sufficient to produce enough differential thermal expansion that superplastic forging pressure is obtained, the hydraulic motor operating to hold the mold closed against this pressure.

Only a small amount of superplastic forging is necessary to replicate the surface finish of the mold wall on to the ceramic surface, and greater than this small amount is not necessary, and is not desired, since otherwise the overall dimensions of the body will be changed to an unwanted amount, as is the case with conventional superplastic forging, which involves dimension changes of at least 30%.

Figure 11 shows the mold adapted for the production of hollow washers or cylinders, the central hole being produced by a central mandrel or core pin 92. The small amount of superplastic flow that is employed is nevertheless sufficient to ensure that not only the flat surfaces normal to the force are superplastically molded, but the hole faces parallel thereto will also take on the surface finish of the butting pin faces.

A typical process as employed to produce square plates of side 5 cm by 5cm and 0.375mm (0.015in) thickness will involve heating of the sintered pieces in the mold to the process temperatures of 1250°C over a period of about 30 minutes. The mold is held at this temperature for a period of about 60-120 minutes to ensure that the molding is complete; with the molding complete the pressing force is removed and cooling of the mold is then allowed to take place, the ceramic plates being allowed to cool down to about 120°C over a period of about 120-180 minutes, when they can be removed from the mold. The mold

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pressures required during the process will usually be in the range of 10 to 50 MPa (1500 to 7500 p.s.i.).

The mold parts are preferably of refractory metal or graphite which has been chemical vapor deposition (CVD) coated with a thin film of refractory metal, since it is possible with current techniques to more readily obtain the superior surface finishes and flatness that is required for the finished parts. Metals of low temperature coefficient of expansion are also preferred to obtain differential thermal expansion of sufficient value. A preferred material for the mold plates for use with alumina is tungsten or thoriated tungsten. The core pin 92 can also be of tungsten, or a high temperature ferritic alloy containing a small amount of dispersed yttria having a larger coefficient of expansion than the ceramic material.

The processes of the invention have been described in connection with the manufacture of thin flat plates and washers, but it will be apparent that they are applicable also to any shape of molded article with which direct production of superior surface finish is desired.

Apparatus for carrying out the mixing and/or homogenisation step referred to above is shown in Figures 1-5, the figures also illustrating in detail the steps of that method. Such an apparatus comprises a frame 10 upon which is mounted a horizontal stationary press platen member 12 comprising a rigid circular disc of high strength material such as steel. A movable press platen member 14 of the same shape, size and material is mounted on the lower end of a hydraulic piston 16 movable in a cylinder 18 and so as to be at all times parallel to the fixed platen member 12. Each platen member has associated with its respective opposed surface a thin flat supplementary disc 20 and 22 respectively that provides two flat horizontal parallel surfaces 24 and 26 that will actually contact the material to be mixed and/or homogenised. These supplementary discs 20 and 22 may be of a non-metallic and non-contaminating pyrolisable material so that any minute particles that are abraded from the discs will be completely removed from the mixed and/or homogenised material upon subjecting it to a subsequent firing step, so that it does not

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matter if such particles become incorporated in the material, which would not be the case if the steel discs 12 and 14 provided the press surfaces. A suitable material is for example ultra high molecular weight, high density polyethylene. The
5 supplementary platen members may however instead be made of tool steel having the lump/pancake contacting surfaces CVD coated with one of titanium nitride, titanium carbonitride, silicon carbide, boron nitride or diamond. The supplementary discs 20 and 22 may be attached to the platens or may be separate
10 therefrom.

A lump 28 of the material to be mixed and/or homogenised, preferably in the shape of a ball as seen in Figure 2, is placed in the centre of the supplementary disc 20 and the hydraulic motor 16, 18 is operated to move the platen members
15 together with a linear motion under high pressure, squeezing the ball between the press surfaces until it has become flattened to a thin flat pancake-like mass that is about 1/2 to 3/4 the diameter of the discs 20 and 22. When the supplementary platen members are not attached to the platen discs the ball 28 will be
20 placed between the members 20 and 22 and the resultant sandwich is then placed between the platen members.

The platen members are moved apart for access to the resultant thin pancake, which is then returned to its ball-like lump form by an operator wearing clean plastic (e.g.
25 polyethylene) gloves, so that again if contaminated by this contact the contaminant is completely removed by the firing step to which the material is eventually subjected. In particular this restoration to ball-like form is produced by moving the periphery of the thin flat pancake toward its centre with a
30 rolling action until the desired shape is attained. The press is then again operated to press the resulting ball back to pancake form, and these steps are repeated as often as is necessary to obtain the degree of mixing and/or homogenisation required. With a few processes ten such repetitions may be
35 sufficient, but others that are difficult to mix, or where uniformity is particularly required, such as high strength ceramics, may require as many as 30 or 40 repetitions. At this time it is believed that more than 50 repetitions will not be

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required to obtain the maximum possible mixing and/or homogenisation.

It is believed at the present time, although I do not intend to be bound by this explanation, that the highly effective mixing action results from the different radially outward velocities of the material as it pressed from the lump to the pancake shape by the linearly moving press platens, the velocity being higher in the middle of the body where it is free to flow and lower adjacent the press surfaces where it tends to be retained by these surfaces, thus producing a radially spiralling movement in the material which is also rolled and mixed three-dimensionally throughout the body of the material.

The press platens 12 and 14 may be 600cm to 1500cm (2 to 5 feet) diameter, while the supplementary platen members 20 and 22 will be of the same diameter; when made of polyethylene as described above the members 20 and 22 will be from 12.5 to 19mm (0.5 to 0.75 in) thick. The pressure required can be in the range 40-1000 metric tons (44-1100 short tons), and will usually be from 40 to 300 metric tons (44 to 330 short tons), or more generally from 3.5 MPa to 35.0 MPa (500 to 5,000 p.s.i) depending upon the application and the composition of the lump 28. Preferably the press mixing process is such that the thickness of the lump to the thickness of the pancake is a ratio in the range 10 to 200. It is found in practice that the pressure required increases exponentially as the pancake decreases in thickness and eventually the available output of the hydraulic motor will be reached; also as the pancake becomes thinner the effectiveness of the mixing decreases until a point is reached at which attempts to decrease it further are not justified.

The apparatus of Figure 5 is similar to that of Figure 1, but in addition a plurality of electrically operated vibrators 30 are mounted on the upper surface of the upper platen 14, the vibrators being connected by respective leads 32 to a junction box 34 and thence to a control circuit (not shown). These vibrators are operated as the platens are pressed together, the resulting vibrations facilitating the radially outward flow of the material so that a thinner pancake can be

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obtained and/or there is an increase in the speed at which the final pancake is obtained. A suitable range of frequency for the vibrations is 100-3,600. With a pair of platens of 600cm diameter, and employing eight vibrators as illustrated, the
5 power consumption of each vibrator should be at least 500 watts.

About 250g to 5kg of the material conveniently is treated at one time. In a specific example the supplementary discs had a diameter of 600cm (2 feet) and a thickness of 12.5mm (0.5in); the lump of material weighed about 300g (10oz) and
10 formed a ball of about 10cm (4ins) diameter. The press had a capacity of 150 short tons and it was found necessary to apply a force of about 100 tons to obtain the pancake shape of suitable thickness of about 5mm (0.2 in).

The following examples show how highly effective is the
15 mixing and/or homogenisation that is obtained using the processes and apparatus of the invention.

A filter press-cake having sub-micrometer alumina (0.3 micrometer average) and 20-25% by weight water as its principal ingredients is of such stiff nature that it cannot be fed to a
20 roller mill or calender, but after three to five press mixing cycles the material feels more pliant when handled and after 10 cycles it has the characteristics of stiff rubber (without crocking when bent) and can now readily be transfer molded without loss of any of the components.

25 Another mixture, again having sub-micrometer alumina as the principal ingredient, was subjected to 30 press-mixing cycles after the addition of a small amount (i.e. about 0.001% by weight) of sub-micrometer lamp black. The degree of uniformity obtained was such that the surface of the resulting
30 pancake body was of absolutely uniform grey colour with no non-uniformity of colour or gloss observable. Examination with a microscope was not able to detect any separate carbon particles or agglomerates.

When "green" polycrystalline alumina parts were
35 sintered after having been prepared according to the invention they unexpectedly reached a theoretical maximum density of 3.98 g/cc after sintering without the need for the usual subsequent expensive hot isostatic pressing (HIP) process indicating that the sintered material was void-free.

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INDEX OF REFERENCE SIGNS

	10	Mixing Press frame
	12	Mixing Press Lower Platen
5	14	Mixing Press Upper Platen
	16	Hydraulic Motor Piston
	18	Hydraulic Motor Cylinder
	20	Lower Supplementary Platen
	22	Upper Supplementary Platen
10	24	Upper Supplementary Platen Surface
	26	Lower Supplementary Platen Surface
	28	Lump or Ball of Pasty Material
	30	Electrical Vibrators
	32	Electrical Leads
15	34	Electrical Junction Box
	36	Reservoir for Slurry
	38	Stirring Propeller
	40	Stirring Motor
	42	Connecting Pipe
20	44	Pressure Pump
	46	Connecting Pipe
	48	Ultrasonic Treatment Cell
	50	Connecting Pipe
	52	Return Valve
25	54	Outlet Valve
	56	Ultrasonic Vibrator Frame
	58	Pressure Gauges
	60	Ultrasonic Vibrator Elements
	62	Molding Press Frame
30	64	Molding Press Hydraulic Cylinder
	66	Furnace Casing
	68	Lower Furnace Support
	70	Lower Furnace Platen
	72	Upper Furnace Support
35	74	Upper Furnace Platen
	76	Insulating Layers
	78	Heater Elements
	80	Lower Recessed Mold Plate

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INDEX OF REFERENCE SIGNS

	82	Upper Mold Plate
	84	Molding Recesses In Lower Mold Plate
5	86	Articles Molded by Mold
	88	Lower Surfaces Mold Recesses
	90	Lower Surface Upper Mold Plate
	92	Mold Centre Pin

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CLAIMS:

1. A method for the mixing and/or homogenisation of pasty material comprising the steps of:
 - 5 a) placing a mass of the pasty material in the form of a lump between two relatively movable press members having opposed respective parallel press surfaces;
 - b) moving the press members linearly toward one another under pressure so that the press surfaces engage the pasty material and continuing the movement until the lump is flattened to a thin pancake-like form;
 - 10 c) moving the press members away from one another to permit access to the resultant thin pancake;
 - d) accessing the thin pancake and returning the pasty material to the form of a lump by inward rolling movement of the pancake periphery toward its centre; and
 - 15 e) repeating steps a)-d) until the desired amount of mixing and/or homogenisation has been obtained.
- 20 2. A method as claimed in claim 1, wherein the steps a)-d) are repeated from 10 to 50 times.
3. A method as claimed in claim 2, wherein the steps a)-d) are repeated from 20 to 30 times.
- 25 4. A method as claimed in any one of claims 1 to 3, wherein the ratio of the thickness of the lump to the thickness of the pancake is in the range 10 to 200.
- 30 5. A method as claimed in any one of claims 1 to 4, wherein the pressure applied is in the range 40-300 metric tons.
6. A method as claimed in any one of claims 1 to 5, wherein the pressure applied is in the range 3 MPa to 35 MPa (500 to 5,000 p.s.i).
- 35 7. A method as claimed in any one of claims 1 to 6;

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wherein the platen surfaces are provided by respective supplementary platen members mounted on the press platens.

8. A method as claimed in claim 7, wherein the
5 supplementary platen members are discs of thickness in the range of 12.5mm to 19mm (0.5 to 0.75 inch).

9. A method as claimed in claim 7 or 8, wherein the
10 supplementary platen members are of steel having the lump/pancake contacting surfaces coated with one of titanium nitride, titanium carbonitride, silicon carbide, boron nitride and diamond.

10. A method as claimed in any one of claims 1 to 8,
15 wherein the pasty material of the lump/pancake is subjected to a firing step subsequent to the mixing and/or homogenisation steps, and the platen surfaces that engage the lump/pancake are formed of a material that will be removed from the pasty material upon subjecting the last mentioned material to the
20 subsequent firing step.

11. A method as claimed in claim 10, wherein the platen surfaces are of high molecular weight high density polyethylene.

25 12. A method as claimed in any one of claims 1 to 11, including the further steps of:

preparing a sintered body of the powdered material with grain size 1 micrometer or less so as to permit superplastic forging thereof;

30 depositing the sintered body in a mold having at least one finished mold surface of the surface finish required for a corresponding surface to be finished of the molded article, the body in the mold being heated to a superplastic forging temperature of at least $0.5M$ where M is the melting temperature
35 of the material;

while the sintered body in the mold is at the said forging temperature applying pressure thereto of a value, for a time, and in a direction such as to produce superplastic forging

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and molding of at least the said body surface to be finished in contact with the said finished mold surface so as to impart the same surface finish to the body surface to be finished; and

the superplastic forging and molding being carried out
5 to obtain a superplastic shear deformation of the sintered body of not more than 5%.

13. A method as claimed in claim 12, wherein the superplastic forging and molding is carried out to obtain a
10 superplastic shear deformation of the sintered body of between 1% and 3%.

14. A method as claimed in claim 12 or 13, wherein the sintered body is sintered to at least 99.5% of theoretical
15 density.

15. A method of manufacturing molded articles from powdered material including the steps of:

preparing a sintered body of the powdered material with
20 grain size 1 micrometer or less so as to permit superplastic forging thereof;

depositing the sintered body in a mold having at least one finished mold surface of the surface finish required for a corresponding surface to be finished of the molded article, the
25 body in the mold being heated to a superplastic forging temperature of at least 0.5M where M is the melting temperature of the material;

while the sintered body in the mold is at the said forging temperature applying pressure thereto of a value, for a
30 time, and in a direction such as to produce superplastic forging and molding of at least the said body surface to be finished in contact with the said finished mold surface so as to impart the same surface finish to the body surface to be finished; and

the superplastic forging and molding being carried out
35 to obtain a superplastic shear deformation of the sintered body of not more than 5%.

16. A method as claimed in claim 15, wherein the

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superplastic forging and molding is carried out to obtain a superplastic shear deformation of the sintered body of between 1% and 3%.

5 17. A method as claimed in claim 15 or 16, wherein the sintered body is prepared by the steps of:

preparing a slurry of the powdered material with a liquid suspension medium; and

10 stirring the slurry to obtain a physically uniform slurry of particle size 1 micrometer or less.

18. A method as claimed in claim 17, and including the step of subjecting the stirred slurry to the effect of ultrasonic energy to increase its chemical uniformity.

15

19. A method as claimed in claim 15 or 16, and including the steps of:

preparing a slurry of the powdered material with a liquid suspension medium; and

20 subjecting the slurry to the effect of ultrasonic energy to obtain a physically uniform slurry of particle size 1 micrometer or less and to increase its chemical uniformity.

20. A method as claimed in any one of claims 15 to 19, wherein the sintered body is prepared by the steps of:

25 a) placing a mass of the pasty material in the form of a lump between two relatively movable press members having opposed respective parallel press surfaces;

b) moving the press members linearly toward one another under pressure so that the press surfaces engage the pasty material and continuing the movement until the lump is flattened to a thin pancake-like form;

c) moving the press members away from one another to permit access to the resultant thin pancake;

30 d) accessing the thin pancake and returning the pasty material to the form of a lump by inward rolling movement of the pancake periphery toward its centre; and

e) repeating steps a)-d) until the desired amount of

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mixing and/or homogenisation has been obtained.

21. A method as claimed in claim 20, wherein the mass of
pasty material is prepared by the steps of:

- 5 a) preparing a slurry of the powdered material with a
liquid suspension medium;
b) removing liquid suspension medium from the slurry to
obtain a pasty material of a solids content of from 70% to 90%.

10 22. A method as claimed in any one of claims 15 to 21,
including the step of preparing by transfer molding a molding
body from which the sintered body is prepared.

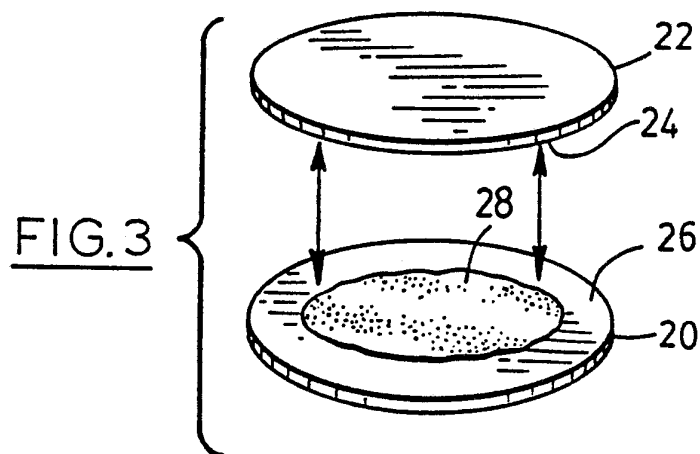
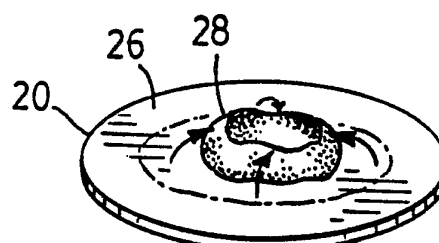
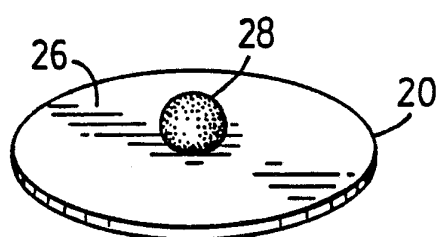
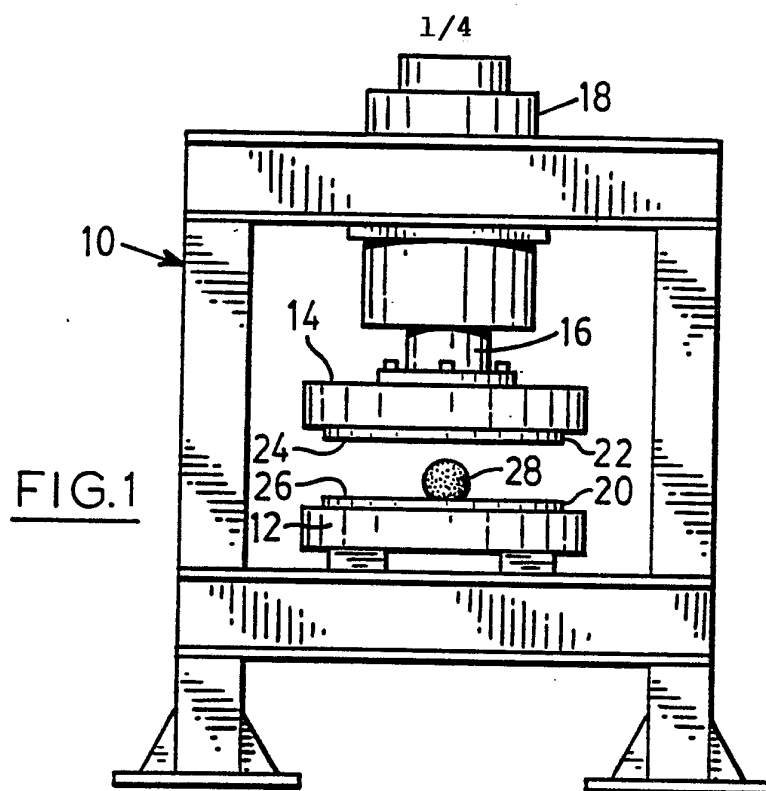
23. A method as claimed in any one of claims 15 to 22,
15 wherein the sintered body is prepared using rate controlled
sintering of a green body of the powdered material to maintain
the grain size of the body at 1 micrometer or less.

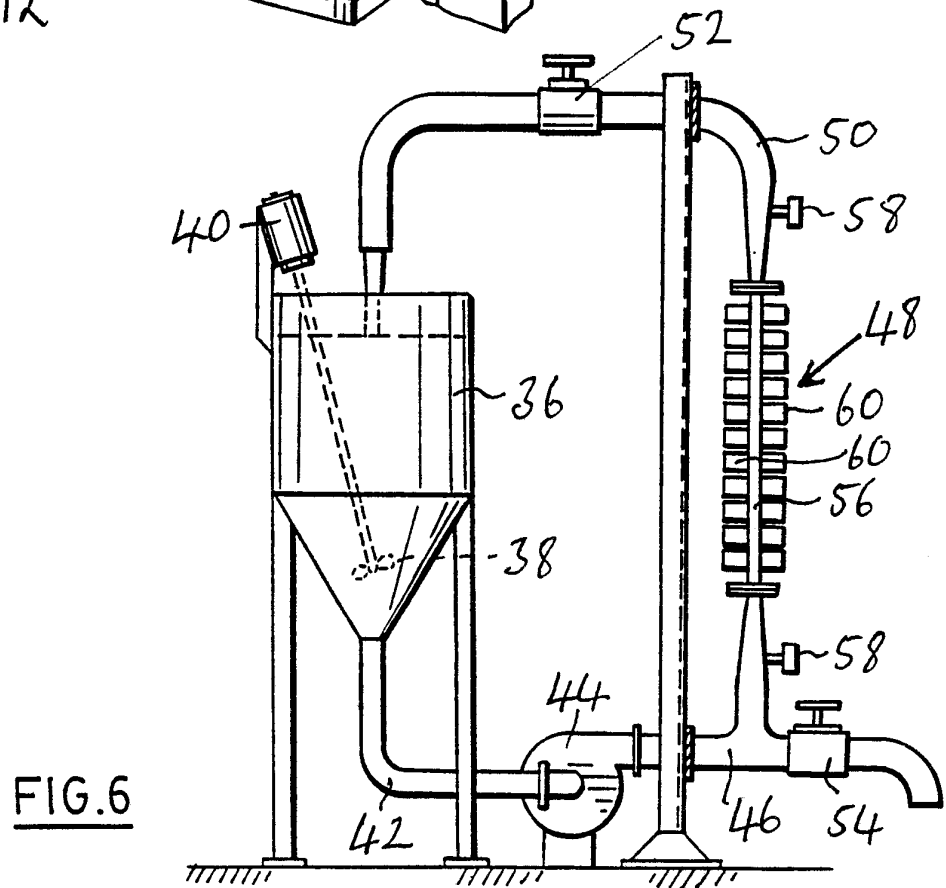
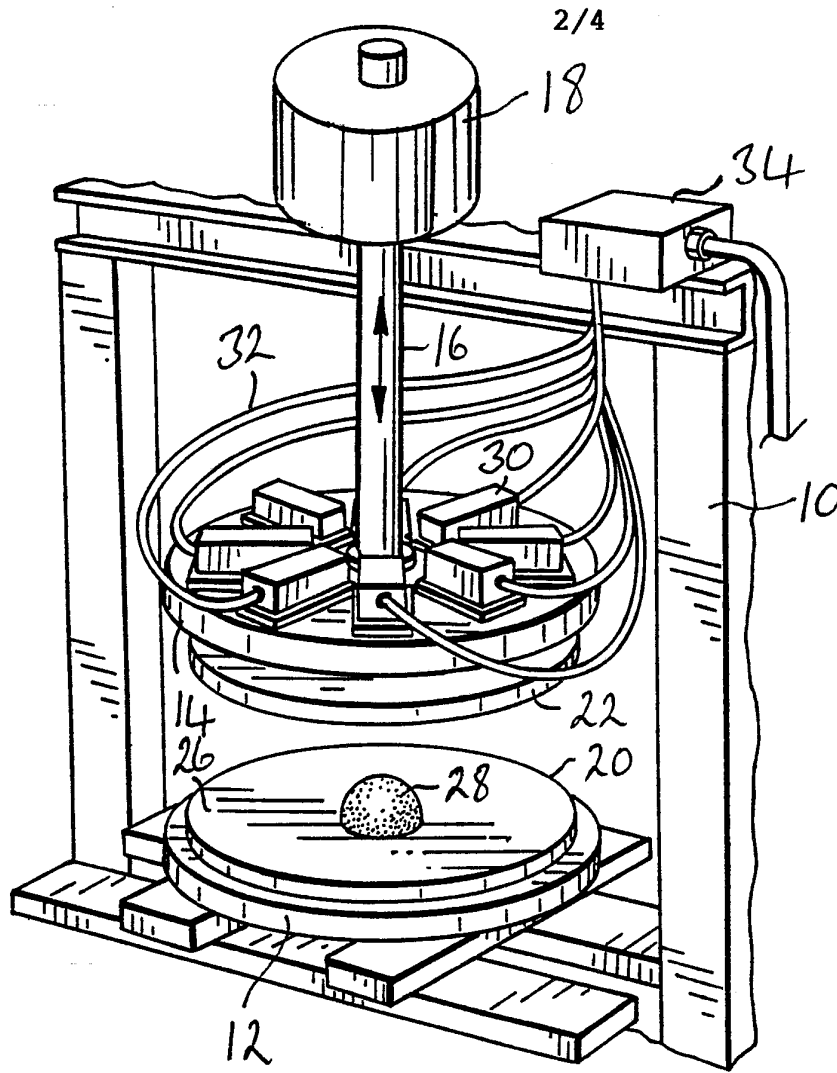
24. A method as claimed in any one of claims 15 to 23,
20 wherein the sintered body is sintered to at least 99.5% of
theoretical density.

25. A method as claimed in any one of claims 15 to 24,
wherein the sintered body is heated in the mold and the mold is
25 not closed until the sintered body has reached the temperature
0.5M.

26. A method as claimed in any one of claims 15 to 24,
wherein the sintered body is heated in the mold with the mold
30 closed, and pressure required for the superplastic forging and
molding is produced by differential greater expansion of the
sintered body than of the mold cavity.

27. A sintered body when prepared by any of the methods of
35 claims 1 to 26.





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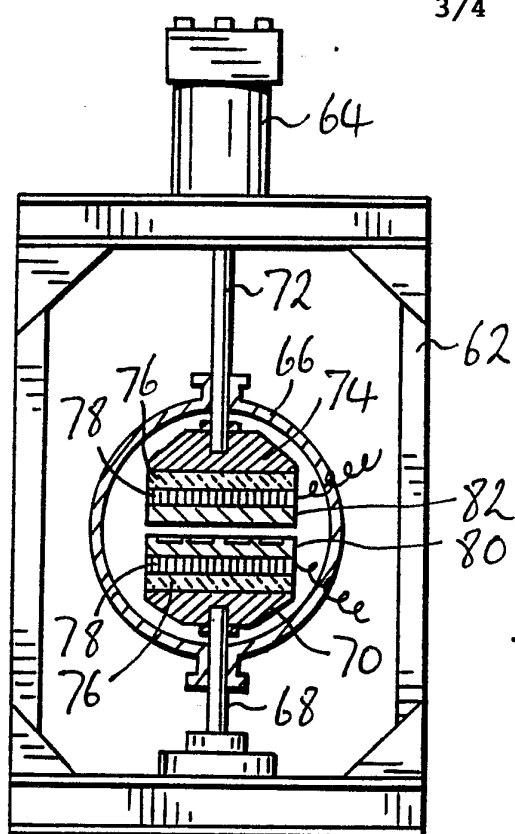


FIG. 7

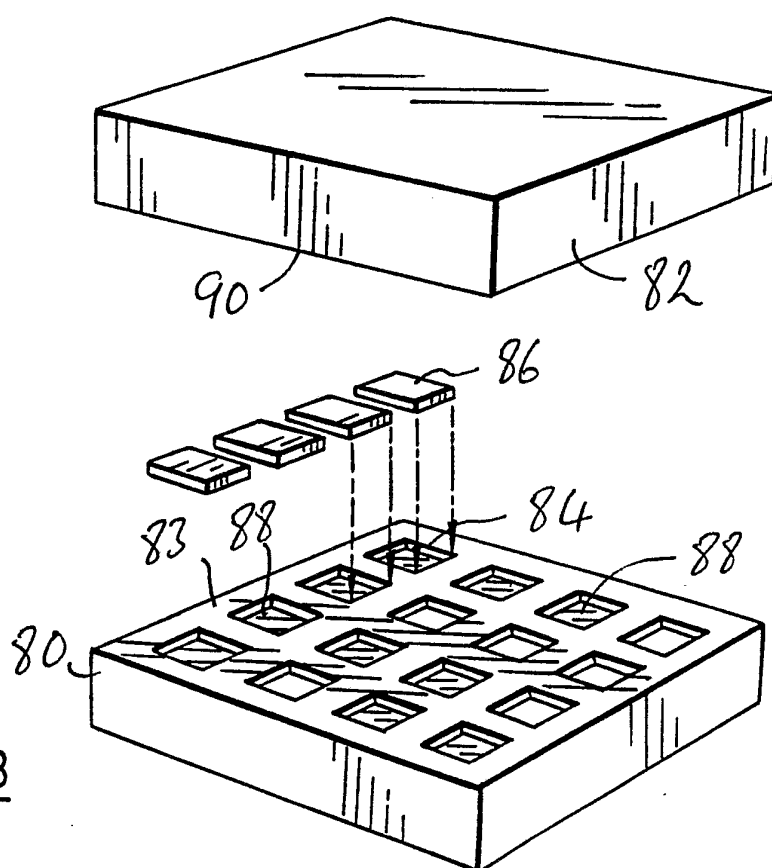


FIG. 8

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