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(72) **Inventeur/Inventor**:
GOLDBERGER, WILLIAM M., US

(73) **Propriétaire/Owner**:
SUPERIOR GRAPHITE CO., US

(74) **Agent**: FINLAYSON & SINGLEHURST

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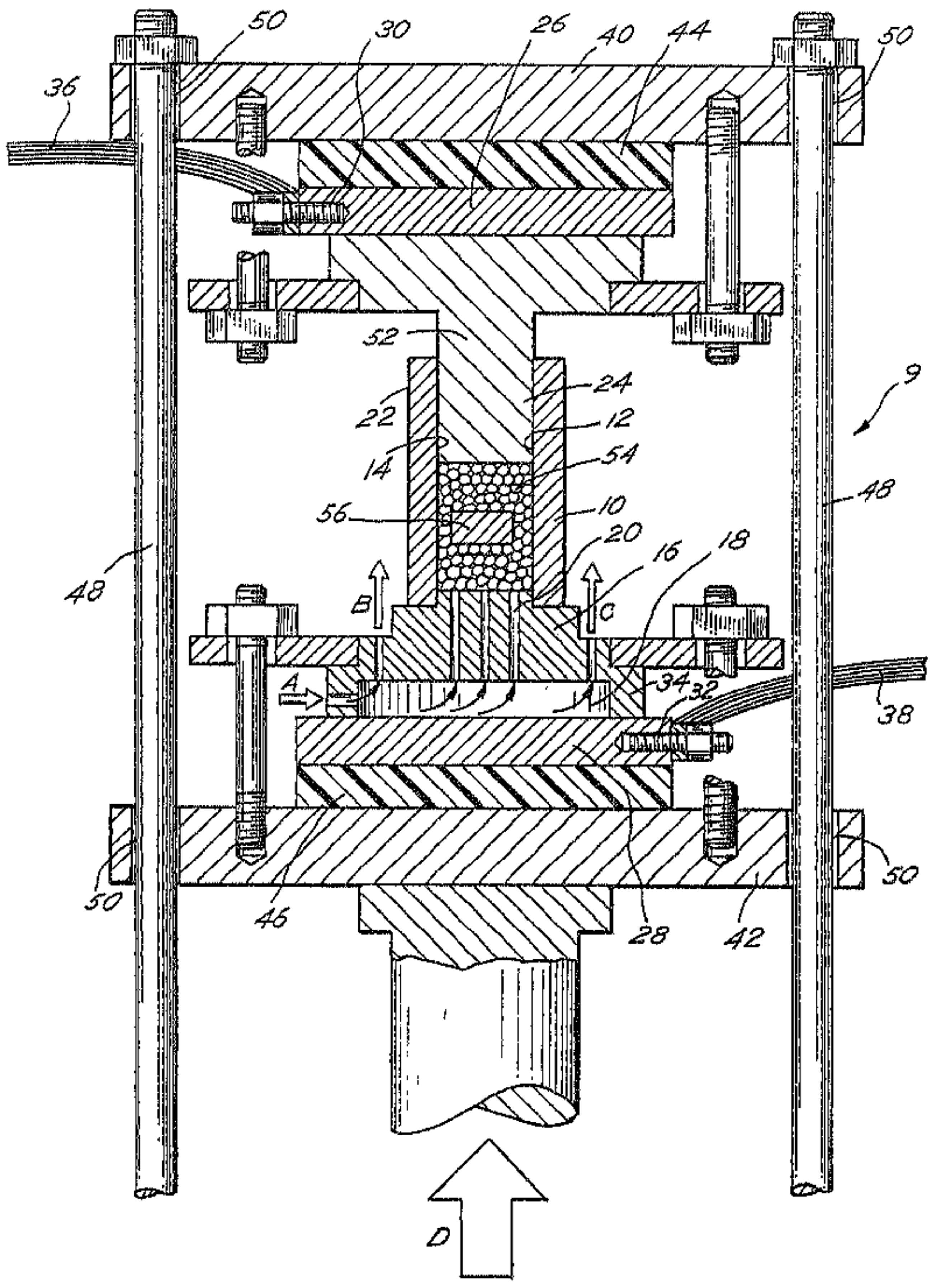
(54) Titre : METHODE D'ELECTROCONSOLIDATION D'UNE PIECE PARTICULAIRE PREFORMEE
(54) Title: IMPROVED METHOD FOR ELECTROCONSOLIDATION OF A PREFORMED PARTICULATE WORKPIECE



(57) Abrégé/Abstract:

The present invention comprises an improved method of consolidating particulate materials or combinations of such materials into shaped products of very low porosity. High compaction pressures are applied at temperatures in the range of sintering temperature of the materials being consolidated to achieve essentially complete densification at extremely rapid processing rates. Electrothermal heating is utilized to accomplish these results. Difficult materials such as silicon carbide, boron carbide and other very high melting point materials may be densified by these techniques.

IMPROVED METHOD FOR ELECTROCONSOLIDATION OF A PREFORMED PARTICULATE WORKPIECE

ABSTRACT OF THE DISCLOSURE

The present invention comprises an improved method of consolidating particulate materials or combinations of such materials into shaped products of very low porosity. High compaction pressures are applied at temperatures in the range of sintering temperature of the materials being consolidated to achieve essentially complete densification at extremely rapid processing rates. Electrothermal heating is utilized to accomplish these results. Difficult materials such as silicon carbide, boron carbide and other very high melting point materials may be densified by these techniques.

IMPROVED METHOD FOR ELECTROCONSOLIDATION OF A PREFORMED PARTICULATE WORKPIECE

BACKGROUND OF THE INVENTION

The present invention is directed to a method of consolidating particulate metals, ceramic materials, or combinations of such materials into shaped products of very low porosity. More specifically, this invention provides a means to apply high compaction pressures at temperatures in the range of sintering temperature of the materials being consolidated to achieve essentially complete densification at extremely rapid processing rates as compared with prior art technologies. Moreover, because this invention employs a method of electrothermal heating generally referred to as "charge-resistor" heating, the temperatures that can be obtained by the process of this invention are well above the requirements for even the most refractory and heretofore difficult to densify materials, such as silicon carbide, boron carbide and other very high melting point materials.

Processes for making dense metallic and/or ceramic articles from their powders are well established in industrial practice of the prior art. It is possible, for example, by the method known as "hot pressing," to place the powder between two cylindrical pistons contained within a cylindrical chamber having only a slightly greater diameter than the pistons, and by application of heat and pressure directly to the powder, the powder can be formed into a highly dense cylindrical billet. Because the method applies an external pressure directly to the material at or near its sintering temperature, hot pressing will yield consolidated product of higher density than if the powder material is densified by pressureless sintering. Hot pressing is a relatively simple prior art method to achieve essentially complete densification and is widely used to make many articles in present commercial use. However, because high temperatures are needed to consolidate high melting point metal alloy powders and the recently developed high performance ceramic materials, the dies and plungers used for hot pressing must be made of a material capable of withstanding the required temperature. Graphite is the most practical material and is commonly used in commercial hot pressing of ceramics. To avoid oxidation of graphite tooling, the hot processing apparatus must be enclosed within a controlled atmosphere chamber, and shielded therein by inert gases. Often, a vacuum is also pulled on the chamber containing the hot pressing apparatus to allow for the removal of reactive gases that may evolve during heating of the material.

A major disadvantage of this method of consolidation is that the cycle time or hot pressing increases with temperature, making the process slow at very high temperature. It is a further disadvantage that in order to utilize effectively the space available in a hot pressing furnace, it is necessary to assemble a series of parts into a "stack". This procedure can be intricate and not readily adapted to automated production.

Even more disadvantageous from the standpoint of commercial production of high performance structural ceramics is that it is impossible to use simple uniaxial hot pressing to make parts of complex shape. For example, turbine rotors that have intricate curved shapes and substantial variation in the thickness cannot be hot pressed.

To make an article of complex shape the processing that is generally used involves "pre-forming" the powder into a partially densified article having the desired shape of the finished part, then further consolidating the pre-form in a second step. Methods commonly used to make the pre-form include die pressing, slip casting, injection molding and extrusion. Pre-forms can then be further consolidated by one or a combination of operations that include cold isostatic pressing, hot pressing, hot isostatic pressing (HIPING), cold and hot forging, hot extrusion and pressureless sintering.

Hot isostatic pressing or HIPING involves sealing a pre-form in an evacuated flexible container and inserting the cladded part into a pressure vessel, then applying pressure while heating to the sintering temperature. The container can be a thin metal sheath that can be welded, evacuated and sealed. If the metal cladding material is properly selected, it will deform to the shape of the preform and transmit pressure uniformly and isostatically to the part being consolidated. Pressure is applied by compression of the gas in the surrounding chamber. For ceramic components that require very high temperatures to achieve consolidation, for example silicon carbide parts, a metal sheath may be impractical and means to encapsulate the part in a glass composition has been developed.

Hot isostatic pressing does provide a means to consolidate metal and ceramic preforms into dense articles of complex shape and there is a growing use of HIPING in commercial production of powdered metal parts and ceramic components. However, the major use of HIP has been to densify cast metals and to consolidate powder metal parts. HIP technology can be applied to ceramic materials including the high temperature non-oxide ceramics, such as silicon carbide; but the costs are very high. Temperatures in excess of 2000°C are needed at pressures of 30,000 psi or higher. As in hot pressing, HIPING entails long cycle times. Because the cost of high pressure equipment and systems are higher than for hot pressing, HIPING is more expensive. There has therefore been increasing interest in other methods that would allow production of ceramic components of complex shape at lower cost.

Yet further, one method receiving extensive study by ceramicists is pressureless sintering. Pressureless sintering involves making preforms of the part from ultra-fine, sinter-active ceramic powder, for example by injection molding or cold isostatic pressing, then heating the preform to a temperature approaching the melting point of the material(s) to be sintered, causing a shrinkage and consolidation to the desired final size and shape. Pressureless sintering not only can consolidate complex and intricately shaped parts but it offers the obvious advantage of adaptation to continuous and easily automated production with inherently lower cost of mass production.

Despite already noted advantages of the pressureless sintering method, technical factors may limit the ability to utilize this process to make certain high performance structural ceramic components from certain powdered ceramic materials. This is particularly true in the case of the high melting temperature non-oxide ceramic materials such as the nitrides, carbides, and borides. For example, to achieve a near theoretical density part by pressureless sintering of silicon carbide powders, it is mandatory to use a silicon carbide powder that is all substantially below 1-2 micron particle size, and meeting close chemical specifications with regard to contained oxygen, carbon and trace elements.

Deviation from these specifications will lead to failure to obtain an essentially pore-free and homogeneous flaw-free structure absolutely necessary to obtain the high strength characteristics required in aircraft or automotive engine turbine rotors. Thus, the production of suitably qualified powders meeting the rigorous demands for pressureless sintering involves intricate and careful control that results in relatively high cost starting raw material powders. Furthermore, even with the most careful control during production of powders, pressureless sintering at high temperature requires a finite time during which the preformed powder compact must remain at the sintering temperature to allow for full shrinkage and densification. Inherent with the sintering process is the tendency for growth of the grains causing departure from the idealized ultra-fine, equi-axed microstructure that offers the highest material strength. Powders that undergo crystal phase transformation at or near the sintering temperature are particularly susceptible to grain growth and a resulting decrease in strength properties. This effect is made more pronounced with increased residence time at the sintering temperature.

It can be noted that very high temperatures are needed to sinter materials that are candidates for high performance engine components. As stated, silicon carbide requires temperatures above 2000°C to achieve a high degree of densification by pressureless sintering. Although it would be highly desirable from the standpoint of minimizing grain growth to rapidly heat a preform to the sintering temperature and limit the time at temperature to no longer than several minutes, and, possibly to residence times of no more than several seconds, there are a number of practical limitations to doing this by a pressureless sintering process. First, sintering furnaces of conventional design are simply not suited to a quick entry or withdrawal of the material being sintered. More important, however, is the fact that gases are likely to evolve from the preform during heat-up due to a combination of desorption, decomposition and chemical reaction. Too rapid a heat-up rate and associated gas evacuation rate can cause mechanical stresses that would fracture the part. And thirdly, too rapid a heating and/or cooling could also cause fracture due to differential expansion or contraction, referred to as "thermal shock". The limits of temperature rise rate and cooling rate during pressureless sintering are different for different materials and are dictated by the specific material being processed and the size and shape of the part.

However, it should be noted in regard to the limits of temperature rise rate and the speed of the sintering cycle that substantially higher cycle rates are possible when the material is being subjected to pressure, for example as in hot pressing. Pressure minimizes cracking due to gas evolution and, if maintained during the densification cycle it allows a substantially closer approach to achieving theoretical density then by pressureless sintering.

Thus, the present state of the art can be summarized, as follows: the pressureless sintering method for the manufacture of advanced materials by consolidation from powders, and particularly for making high performance ceramics, represents the most attractive method from the standpoint of high volume-low cost production. However, the mechanical properties obtained in pressureless sintered materials are generally not as good as in materials made by application of pressure during sintering, as is the case for hot pressed and/or HIPED products. But these latter methods are either unsuited for making parts of complex shape and/or are very slow and unable to be easily or fully automated; thus, they are very expensive.

It is therefore one material object of the present invention to overcome many of the difficulties of the prior art methods, and more particularly to provide a means for extremely rapid sintering under pressure to achieve consolidated parts of low porosity and having a flaw-free and ultra-fine grain structure.

It is a further object of the present invention to be able to accomplish these basic objectives even with materials that require temperatures well above 2100°C.

It is still further the purpose of the present invention to accomplish the above objectives within seconds using temperature rise rates in excess of 50°C/sec.

Moreover, it is the purpose of this invention to consolidate preformed materials of complex shape under compaction pressures approaching isostatic compaction conditions. It is still further the purpose of this invention to accomplish these objectives using relatively inexpensive apparatus that is simple in construction and operation and that can be readily adapted to automated and continuous high volume production.

It is recognized that the above objectives of the present invention have been addressed by previous workers. In that regard, descriptions of processes intended as improvements in manufacture of parts by consolidation of powders have been described in the technical literature and in previously issued patents. Most pertinent are the patents issued to <u>Lichti</u> and <u>Hofstatter</u> (U.S. Pat. Nos. 4,539,175 and 4,640,711). These workers have demonstrated that simple tooling similar to that used in hot pressing can in fact be used to consolidate articles of complex shape by first surrounding the article by a spherically shaped particulate medium which has sufficient resiliency to be deformed under high compaction pressures without excessive breakage and thereby transmit the compaction pressure in a nearly isostatic manner to the part being consolidated. The <u>Lichti-Hoffstatter</u> patents (U.S. Pat. Nos. 4,539,175 and U.S. 4,640,711) note the advantages provided by using Superior Graphite Co. spherical graphitic carbon product (9400 Series) as the preferred pressure transmitting particulate medium.

Although the consolidation methods of Lichti and Hofstatter theoretically may offer significant advantages in consolidation of preformed articles, it has in actual practice been found quite difficult to apply the described procedure for materials requiring very high temperatures for consolidation; for example, for materials that must be heated to above 1500°C (2732°F) to achieve densification. U.S. Pat. No. 4,539,175 to Lichti et. al. notes that the consolidation process takes place after the heated preform is placed in a bed of previously heated carbonaceous particles (Col. 4, lines 35 *et* seq.). It is further stated that although the graphite particles can be heated inductively to 4000°F (2204°C), oxidation is significant above 800°F. Hence, it follows that the operation step at temperatures approaching 4000°F (2204°C) would become extremely difficult. U.S. Pat. No. 4,539,175 specifically notes that heating to the necessary temperature is done before compaction.

U.S. Pat. No. 4,640,741 describes again the consolidation process of their invention and notes the use of a non-graphitic spherical carbon and mixtures of graphitic and non-graphitic spherical carbon and mixtures of spherical carbon and/or spherical graphitic carbon and ceramic particles as the pressure transmitting medium. U.S. Pat. No. 4,640,741 is again specific in noting that the preform and the bed of particles are to be at elevated temperature before pressurization. Thus, the patented processes of Lichti and Hofstatter require that both the particulate medium and the pre-form be preheated independently and then individually transported to the compaction apparatus in sequence to allow the pre-form to be immersed within the medium prior to compaction. Such transfer of materials after heating becomes extremely difficult at temperatures needed to consolidate non-oxide ceramics, such as silicon carbide (1900°-2150°C), and apparatus to accomplish the transfer is complex, expensive and wasteful of energy.

It is further recognized that a process has been reported by Eliezer and co-workers at the University of Texas referred to as High-Energy, High-Rate Consolidation which utilizes a very high energy electrical discharge, not through a bed, but rather directly to the pre-form while applying compaction pressure to the preform. In this process, electrical energy is transmitted directly through the material being consolidated, and thus can be used only to consolidate those materials having sufficient electrical conductivity. By using a suitably electrically conductive particulate medium, the present invention is not so restricted and materials with no electrical conductivity can be consolidated by the process hereof. Yet further, since the process described by Eliezer et al. is conducted in a manner similar to hot pressing, it is no more suited than hot pressing for making components of complex shape.

In view of <u>Lichti</u> and <u>Hofstatter</u> and Eliezer et al., it is still another objective of the present invention to utilize the principle of consolidation by compacting a free flowing solid particulate medium as a near isostatic pressure transmitter, but to accomplish heating and compaction essentially simultaneously by a rapid, convenient and energy efficient means.

It is a further object of the present invention to include embodiments utilizing a bed material which is not confined to the narrowly specific bed material of the prior art.

SUMMARY OF THE INVENTION

The present invention comprises an improved method of consolidating workpieces preformed from particulate, powdered, sintered, fibrous, spongiose, or other solid containing material capable of consolidation. The steps of such improved process include providing a bed of electrically conductive, flowable particles within a contained zone. Next, the preformed workpiece is positioned in such bed of electrically conductive, flowable particles. Next, sufficient compaction of the electrically conductive medium for good electrical conductivity is provided. Thereafter, electrical energy is applied to the electrically conductive, flowable particles within the bed in an amount sufficient to heat the bed to the consolidation temperature for the workpiece. Finally, pressure is applied to the bed of the electrically conductive flowable particles in an amount sufficient to effectuate substantial consolidation of the work piece.

Additional details of the improved method of the invention will be better understood with reference to the following brief description of the drawing, detailed description of preferred embodiments, appended claims and accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

The improved methods of the present invention may be better understood with reference to the accompanying drawing, and in which:

Fig. 1 depicts a partially longitudinal cross-sectional view of an apparatus suitable for carrying out the improved method of the present invention, including a cylindrical vertical sleeve with a ceramic coating on the interior thereof, which sleeve is subjected to the compressive force of a graphite piston disposed for longitudinal movement therein for compressing the particulate contents of such sleeve; and

Fig. 2 is a graphical representation of pellet density (in g/cc) graphed against supplied power (KW) and showing the resulting density (as a percentage of theoretical density).

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention comprises an improved method of consolidating work pieces preformed from particulate, powdered, sintered, fibrous, spongiose, or other solid containing material capable of consolidation. The steps of such improved process include providing a bed of electrically conductive, flowable particles within a contained zone. Next, the preformed workpiece is positioned in such bed of electrically conductive, flowable particles. A suitable pressurization is provided to the bed material to allow for adequate electrical contact of the bed particles. Thereafter, electrical energy is applied to the electrically conductive, flowable particles within the bed in an amount sufficient to heat the bed to the consolidation temperature for the workpiece. Finally, pressure is applied to the bed of the electrically conductive flowable particles in an amount sufficient to effectuate substantial consolidation of the work piece. Such pressure may be uniaxially applied in certain preferred embodiments.

In preferred embodiments of the improved method hereof, the electrically conductive flowable particles of the bed may preferably consist primarily of flowable and resiliently compressible carbonaceous particles in the form of beads, which may have outwardly projecting nodules thereon, and at least some beads may have surface fissures thereinto.

The particular workpiece may comprise silicon carbide, boron carbide, and/or combinations of other carbides and/or in conjunction with metals.

The amount of electrical energy applied to the bed of conductive flowable particles should in preferred embodiments be sufficient to raise the temperature of such bed to a temperature in excess of approximately 2200°C, for certain uses, such as ferrous-based materials, although lower temperatures (such as approximately 1000°C) may be adequate for other materials (such as oxides, powdered metals, non-ferrous materials, etc.). Further preferred embodiments provide for such temperature rise in less than approximately 60 seconds.

The electrically conductive bed is substantially electrically isolated from its surroundings in preferred embodiments. Also in such embodiments, a supply of inert gas is inputted and maintained within the bed prior to and during the application of electrical energy to the bed.

Such particles of the bed may also comprise a silicon carbided spherical graphitic carbon. Such silicon carbide spherical graphite carbon may comprise substantially spherical particles having a diameter of approximately 0.1 mm. to 0.8 mm. Such silicon carbide spherical graphite carbon may comprise approximately 50% silicon carbide, with substantially the balance thereof comprising free carbon. However, such silicon carbided spherical graphite carbon may have some tendency to sinter, especially in consolidating silicon carbide workpieces. But, such silicon carbided materials may provide more beneficial propreties in certain applications, including more accurate control of resistivity, especially in lower temperature applications.

The electrically conductive flowable particles may in preferred embodiments have an electrical resistivity of approximately 0.012 OHM-in. for some specific uses. Such particles may likewise have a resiliency of approximately at least 50%.

In addition to other materials, the preformed workpiece may include as a binder a phenolic resin binder in an amount equal to provide approximately 2% free carbon after pyrolysis. A compaction pressure of approximately 1,000 psi may be utilized, but greater pressures (such as 2,000 psi) are also beneficially used in other embodiments.

The inert gas utilized may comprise nitrogen, argon, or the noble gases.

The electrical energy applied may comprise approximately 15 volts DC at 800 amps for approximately 30 seconds duration, in some systems, depending on the size of the equipment, the workpiece, configuration and material of the workpiece. These parameters and others may be adjusted by one of ordinary skill in the art without undue experimentation.

Such consolidation may in preferred embodiments constitute approximately at least 80% densification. The preformed work piece may preferably comprise 60% densification prior to the application of electrical energy and pressure thereto. The density of such preformed work piece may be increased in preferred embodiments from approximately 2.01 g/cc to approximately 2.80 g/cc.

Boron may be incorporated into the structure of the particles of the electrically conductive flowable bed, and may constitute 1.75% by weight of electrically conductive flowable particles, in preferred embodiments.

The preformed workpiece may be formed by a variety of techniques in preferred embodiments, including cold compaction, and such cold compaction may be uniaxially applied.

Such preformed workpiece may comprise approximately 1% by weight of a 5% solution of phenolic resin as dissolved in a solvent prior to pyrolysis.

At least approximately 20 KW of electrical energy may be preferably applied to the electrically conductive flowable particles during consolidation of such workpiece.

To accomplish the objectives of the present invention, the particulate medium is selected not only to provide the desired compressibility or resiliency characteristics and temperature stability property described in Lichti and Hofstatter, supra, but also to be a suitably electrically conductive material to enable electrical current to be passed through the compaction assembly, and thereby to allow heating by direct electrothermal resistive heating of the medium during the compaction cycle. Such direct electrothermal heating takes place from within the apparatus and more specifically from within the zone between the compaction plungers where the pre-form is contained. Therefore, there is no need to preheat either the pre-form or the particulate medium or to transfer hot materials from separate auxiliary heaters to the compaction device. It should be evident, therefore, with appropriate design of the compaction chamber and choice of the electrically conductive and resilient particulate medium that extremely high energy release rates are possible. In fact, in the present invention temperatures well in excess of 2200°C are achieved in less than 60 seconds of current flow in a device of the type described.

EXAMPLE I

As an example of the application of the present invention, an apparatus generally as shown in Fig. 1 was assembled comprising a cylindrical vertical sleeve 10 of 2-inches in height having a 2-3/8 inch OD and 1-15/16 inch ID. This sleeve 10 was machined from solid graphite stock. To minimize electrical conduction through the inner surface 12 of sleeve 10 a ceramic coating 14 was applied by painting inner surface 12 with a silicon carbide-containing paint obtained from ZYP Coatings, Inc. Sleeve 10 was placed on a machined graphite support 16 having a plenum chamber 18 into which inert gas (see Arrow A) was admitted through gas inlets 20 comprising an array of small holes drilled vertically from the top which allowed the inert gas to escape plenum 18 and to shield the outside 22 of vertical sleeve 10 from attack by ambient air, as shown at Arrows B, C, D.

A vertical graphite piston 24 of 4-inch height overall was machined from 2-3/4 inch cylindrical stock to a diameter of 1-3/4 inch for entry from above into vertical sleeve 10, as shown in Fig. 1.

Upper and lower copper plates 26, 28 respectively of 1/2 inch thickness containing connected drilled holes to serve as cooling water channels were positioned in direct contact with piston 24 and lower support 34 and served as electrical contactors. In turn, these were connected by electrical cables attached at tap hole connectors 30, 32 to a DC power supply of 600 KW capacity, designated respectively 36, 38.

The above assembly was held between platens 40, 42 of a hydraulic press and electrically insulated by insulating plates 44, 46 made of a composition referred to as "GLASTIC™". Tie down bolts 48 were used to provide a compressive force to the upper and lower assemblies through apertures 50.

EXAMPLE II

A series of experiments was made to determine the ability to consolidate silicon carbide by the improved method hereof. The experiments were conducted by introducing into the sleeve a 75g charge of particulate medium 54 comprising a silicon carbided spherical carbon. This product comprises small spheres of 0.1 to 0.8 mm diameter and contains approximately 50 percent SiC with the balance free carbon. The silicon carbided spherical carbon is available from Superior Graphite Co. of Chicago, Illinois and measured 0.012 OHM-in electrical resistivity and a resiliency determined to be 52 percent. Resiliency is defined as the percentage increase in volume of a sample upon release of 10,000 psi compaction pressure.

A 1-inch D x 1/8-in pre-form of silicon carbide in the form of a workpiece 56 was then placed in the bed of particulate such that it was oriented horizontally. The pre-form was made with Superior Graphite Co. silicon carbide (Type HSC 059), contained approximately 2 per cent by weight B_4C, and had been formed by cold compaction using a phenolic resin binder in an amount equivalent to provide about 2 percent free carbon after pyrolysis.

After insertion of the silicon carbide pellet, the plunger was brought into the sleeve and a compaction pressure of 1000 psi was applied by a hydraulic cylinder (unshown) and which raised the lower platen 42 of the press (see large Arrow D in Fig. 1).

Nitrogen flow was started (see Arrow A) and power at 15 volts DC and 800 amps was maintained for 30 seconds. Sleeve 10 was noted to begin to glow red, as did the lower section 52 of plunger 24 that extended above cylindrical sleeve 10.

After cooling and removal of the pellet, it was found that the silicon carbided spherical graphitic carbon had partially sintered around the silicon carbide pellet. The pellet was removed, weighed and measured, and was found to have consolidated from a 60 percent dense material to 80 percent.

EXAMPLE III

A further experiment was conducted using a 1-inch D silicon carbide pre-form made as set forth in Example II, supra, but preheated to 1500°C in a laboratory furnace to fully pyrolyze the phenolic resin binder. In this experiment, the power was applied and maintained at 12 KW input for 1 minute while maintaining a 1000 psi compaction pressure. The pellet after the experiment was found to increase in density from 2.01 g/cc to 2.80

g/cc corresponding to an increase from 60 percent of the theoretical density of silicon carbide to 87.2 percent of theoretical density of silicon carbide.

Thus, although these initial experiments of Examples II and III did not demonstrate complete consolidation of silicon carbide, they did establish a reduction to practice of a novel rapid high energy process for consolidation of high temperature materials.

EXAMPLE IV

The silicon carbides used in some embodiments of the present invention are available from Superior Graphite Co. of Chicago, Illinois under the trademark "HSC". Such HSC silicon carbides have been developed for a wide range of uses including metallurgical additions, refractories, fine abrasive grit, and for high performance ceramics and special heat resistant composite materials.

The HSC 059 grade of silicon carbide is prepared by processing run-of-furnace grade material to remove excess free carbon. This wet milled and chemically purified free flowing powder can be used directly in: metal or ceramic matrix composites, metallurgical and refractory applications, lapping and fine abrasive grit, high purity silicon carbide reaction bonded and pressureless or HIPed sintered ceramics. Table 1 sets forth the specifications of such desired materials.

TABLE 1

TYPICAL PARTICLE SIZE DISTRIBUTION

(MICROMETERS)			Surface area	Bulk Density	Particle Density
d_{90}	d_{50}	d_{10}	Cut-off	(m^2/g:BET)	1.32+0.07gm/cm3
1.3	0.60	0.25	99% < 2	15 +	

TYPICAL CHEMICAL ANALYSIS (Weight Percent)

Component	Range	Typical
Silicon Carbide (beta type)	98.0-99.1	98.5
Oxygen	0.65-0.85	0.80
Nitrogen	0.15-0.25	0.21
Silicon (metallic)	0.1 Maximum	0.03
Sulfur	0.5 Maximum	0.05*
Carbon (free)	0.50-1.00	0.85

TYPICAL SPECTROGRAPHIC ANALYSIS, PPM**

Element	Range	Typ	Element	Range	Typ
Fe	100-500	160	Al	100-350	180
Ca	10-50	15	Zr	50-200	100
Tl	50-150	100	V	100-200	150
Mo	100-300	180	Nl	20-100	80
Mn	10-100	40	Cr	10-50	35
Cu	10-50	20	Co	10-50	10
Mg	<10	<10			

* Sulfur content can be maintained to below 0.03%.

** Elements not shown are below detection level.

EXAMPLE V

Superior Graphite Co. also produces 9400 Series Spherical Graphitic Carbon, which is suitable for other embodiments hereof. This free flowing, high purity spherical graphitic carbon product exhibits unusually high mechanical strength under compressive loading.

The 9400 graphitic carbon is highly resistant to oxidation and chemical attack and has bood molding properties. The fields of use include refractory mixes, hydraulic fracturing proppant, core molds and as a special shot blast media. Oxidation inhibitor can be incorporated into the structure to achieve an extremely high degree of oxidation resistance.

PROPERTIES OF 9400 SERIES SPHERICAL GRAPHITIC CARBON

	TYPICAL RANGE
Carbon Content, Percent	99.9-99.9+
Sulphur Content, Percent	0.01-0.03
Size Range, mm	0.10-0.80(1)
Particle Density, g/cc(2)	1.70-1.85
Electrical Resistivity, ohm-cm x 10_2	3.80-4.60
Resiliency, Percent(3)	

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[1] The particle size range is -20 +150 mesh Tyler Standard screen.

[2] Measured by liquid pycnometry.

[3] Resiliency is the percentage increase in sample volume after release of 10,000 psi (703.7 KB/cm_2 compaction pressure).

EXAMPLE VI

A series of further runs was made to demonstrate consolidation of preforms made of silicon carbide. The apparatus used is set forth in Fig. 1 hereof. In such tests, the particulate medium was 9400 RG grade spherical carbon grain produced by Superior Graphite Co. of Chicago, Illinois, and as described in the prior Examples hereof. This material contained 1.75 percent boron incorporated into the grain structure, and is covered by U.S. Pat. No. 4,560,402 entitled "Metal Bearing Graphitic Carbons."

The 9400 RG product is a preferred material for consolidation of silicon carbide, because boron therein functions as a sintering aid, and its presence in the surrounding grain enhances the densification process. However, other carbided materials which are stable at the reactive temperatures (such as, for example, titanium tungsten, and the rare earth elements) may be used.

The pre-forms hereof were made by cold uniaxial compaction of Superior Graphite Co. HSC 059 grade silicon carbide powder premixed with 110 percent by weight of 5 micron boron carbide and with 5 percent by weight of phenolic resin dissolved in acetone. The pellets were made in a 1-inch D steel die at 20,000 psi to give a green density of 2.14 g/cc corresponding to 66.6 percent theoretical density based on silicon carbide. These pellets were oven dried for 8 hours at 100°C and then baked at 250°C for 8 hours. The pellets were pyrolyzed at 1500°C for 30 minutes to reduce the formation of volatiles during the electroconsolidation process. A slight shrinkage occurred during the pyrolysis step, but because of a corresponding small weight loss, the density of the pellets remained essentially unchanged.

A tabulation of the test conditions and test results is given in Table 2, supra, and shown graphically in Fig. 2 hereof. It is concluded that below about 20 KW applied electrical power, little or no densification had occurred. However, densification was rapid above 20 KW applied power, with pellet density approaching the theoretical density of silicon carbide within several minutes or less.

It should be understood that these data are presented primarily to illustrate that rapid consolidation and densification of a preform of silicon carbide powder has been achieved by the method of this invention. The best conditions for consolidation of silicon carbide and other materials to achieve minimum porosity and an excellent microstructure may require optimizing the main process variables, which can be done based upon such teachings hereof by one of ordinary skill in the art without undue experimentation. These variables include: size of the consolidation chamber, level of applied power, the pressure to be applied, the duration of the consolidation cycle, and the type and electrical characteristics of the particulate pressure transmitting medium. The process conditions table optimized will also depend on the type of material to be consolidated and the size and shape of the pre-form. Also, certain types of shapes of workpieces may call for variation of sequencing and/or compacting pressure.

TABLE 2.

ELECTROCONSOLIDATION OF SILICON CARBIDE POWDER PREFORMS

Test No.	Amount Medium	Electrical			Final Density	
		E. Volts	I. Amps	KW	g/cc	%
		Test Duration 2 Minutes Applied Power				
1	100	8	960	7.68	2.14	66.7
2	125	10	1040	10.40	2.14	66.7
3	125	12	1360	16.32	2.14	66.7
4	125	12	1600	19.20	2.30	71.7
5	125	14	1840	25.76	3.00	93.5
		Test Duration 4 Minutes Applied Power				
8	120	8	1040	8.32	2.14	66.7
9	120	10	1200	12.00	2.14	66.7
10	120	11	1360	14.96	2.14	66.7
11	120	12	1520	18.24	2.24	69.8
12	120	13	1720	22.36	3.05	95.0

Notes

(1) Preform made with Superior Graphite HSC 059 Silicon Carbide Powder.

(2) Preform size 1-in. D x 1/4-in. Thick. Pyrolyzed at 1500 C for 30 minutes to a density of 2.14 g/cc before consolidation.

(3) Pressure Transmitting Medium Superior Graphite 9400 RG Spherical Graphite Grain Containing Boron.

(4) Graphite cylinder 2-in. ID.

(5) Pressure applied: 4,000 psi.

The basic and novel characteristics of the improved methods of the present invention will be readily understood from the foregoing disclosure by those skilled in the art. It will become readily apparent that various changes and modifications may be made in the steps, ranges, parameters and conditions of the improved methods of the present invention, taking into account, inter alia, the nature of the material(s) to be processed, as set forth hereinabove without departing from the spirit and scope of the invention. Accordingly, the preferred and alternative embodiments of the present invention set forth hereinabove are not intended to limit such spirit and scope in any way.

What is Claimed Is:

1. An improved method of consolidating a workpiece pre-formed from particulate, powdered, sintered, fibrous, spongiose, or other solid containing material capable of consolidation, said method including the steps of:

providing a bed comprising a bed material of electrically conductive, flowable particles within a contained zone;

positioning the preformed workpiece in the bed;

sufficiently compacting the bed material to provide for suitable electrical contact of such bed material;

applying electrical energy to said electrically conductive, flowable particles within the bed containing the workpiece sufficient to heat the bed to the consolidation temperature for the workpiece;

applying pressure to such bed of electrically conductive, flowable particles sufficient to effectuate substantial consolidation of the workpiece; and

purging the bed with an inert gas at least during the application of electrical energy to such bed.

2. The improve method of Claim 1 wherein the electrically conductive, flowable particles of the bed comprise carbonaceous particles.

3. The improved method of Claim 1 wherein the electrically conductive, flowable particles of the bed primarily consist of flowable

and resiliently compressible substantially carbonaceous particles in the form of beads at least some of which have outwardly projecting nodules thereon, and at least some beads having surface fissures thereinto.

4. The improved method of Claim 1 wherein said preformed workpiece comprises silicon carbide.

5. The improved method of Claim 4 wherein sufficient electrical energy is applied to the bed of electrical conductive flowable particles to raise its temperature to in excess of approximately 2200°C.

6. The improved method of Claim 5 wherein electrical energy is supplied in an amount sufficient to raise the bed temperature to in excess of approximately 2200°C in less than approximately 60 seconds.

7. The improved method of Claim 1 wherein the electrically conductive bed is substantially electrically isolated.

8. The improved method of Claim 1 wherein the step of purging the bed includes inputting and maintaining a supply of an inert gas within the bed prior to and during the application of electrical energy to the bed.

9. The improved method of Claim 1 wherein the electrically conductive, flowable

particles of the bed are selected from the group consisting of spherical graphite and carbided graphitic material.

10. The improved method of Claim 9 wherein the particles comprise substantially spherical graphite particles having a diameter of approximately 0.1 mm to 0.8 mm.

11. The improved method of Claim 10 wherein said particles comprise approximately 50% silicon carbide, with substantially the balance thereof comprising free carbon.

12. The improved method of Claim 1 wherein the electrically conductive, flowable particles have an electrical resistivity of approximately 0.012 ohm-in.

13. The improved method of Claim 1 wherein the electrically conductive, flowable particles have a resiliency of at least 50%.

14. The improved method of Claim 1 wherein the preformed workplace comprises B_4C.

15. The improved method of Claim 1 wherein the preformed workplace includes phenolic resin binder in an amount equal to provide approximately 2% free carbon after pyrolysis.

16. The improved method of Claim 1 wherein the pressure applied to the electrically conductive, flowable particles is a compaction pressure in the range of approximately 3,000 - 5,000 psi.

17. The improved method of Claim 8 wherein the inert gas is selected from the group consisting of nitrogen, argon and the noble gases.

18. The improved method of Claim 1 wherein the preformed workpiece is consolidated to at least 80% theoretical

density.

19. The improved method of Claim 1 wherein the preformed workpiece is consolidated to approximately 60% theoretical density prior to the application of electrical energy and pressure thereto.

20. The improved method of Claim 1 wherein the density of the preformed workpiece is increased from approximately 2.01 g/cc to approximately 2.80 g/cc.

21. The improved method of Claim 9 wherein the electrically conductive flowable particles of the bed comprise boron incorporated into the structure of the particles.

22. The improved method of claim 21 wherein the incorporated boron comprises approximately 1.75% by weight of the electrically conductive, flowable particles.

23. The improved method of Claim 1 wherein the preformed workpiece is formed by cold compaction.

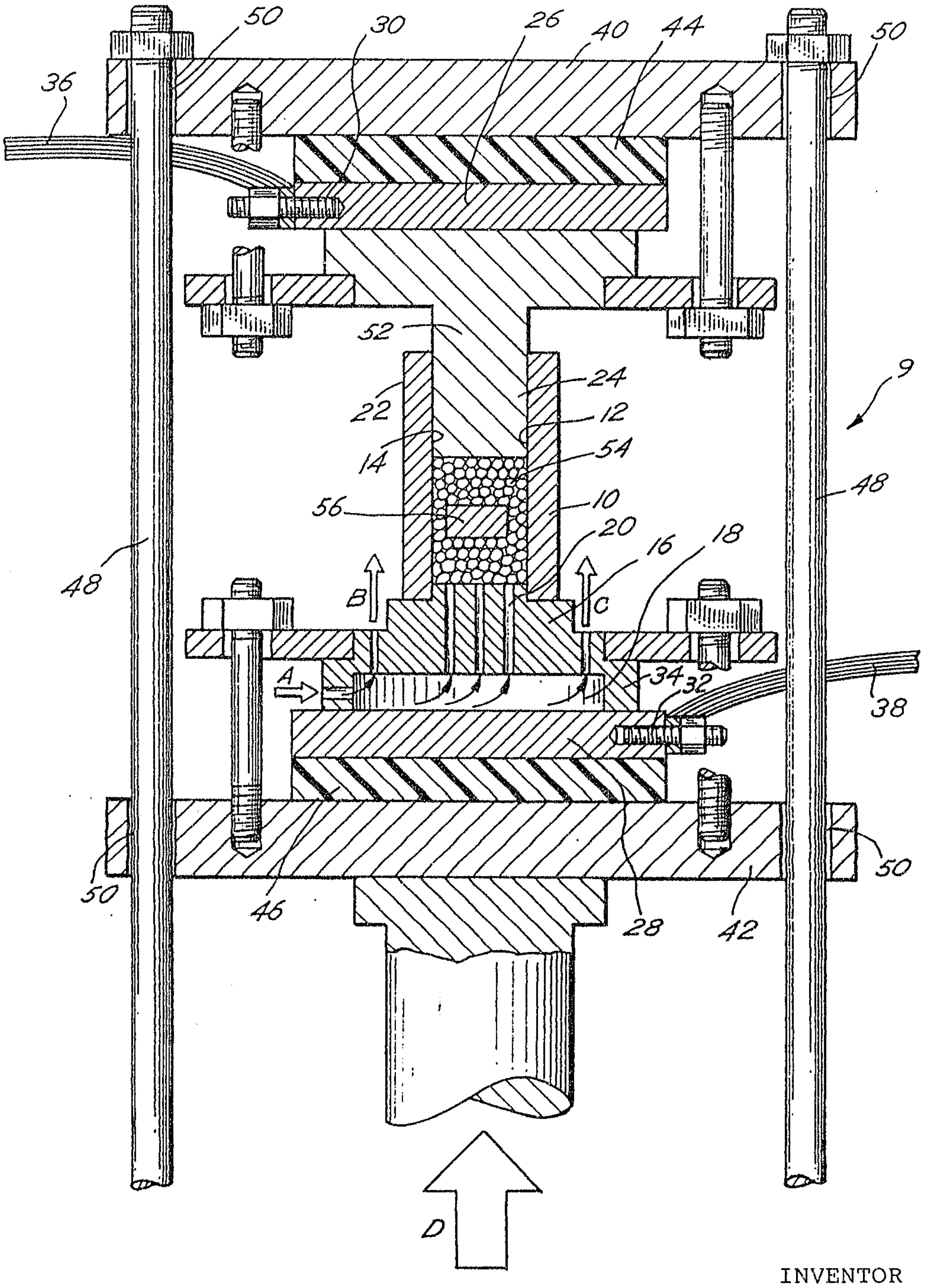
24. The improved method of Claim 23 wherein said bed has an axis and the cold compaction is uniaxially applied to said bed.

25. The improved method of Claim 1 wherein at least 20 KW of electrical energy is supplied to the electrically conductive, flowable particles during consolidation of the work piece.

26. The improved method of Claim 1 wherein the preformed work piece is substantially non-conductive.

27. The improved method of Claim 1 wherein said bed has an axis and such application of pressure to the bed is uniaxially applied to said bed.

Fig.1

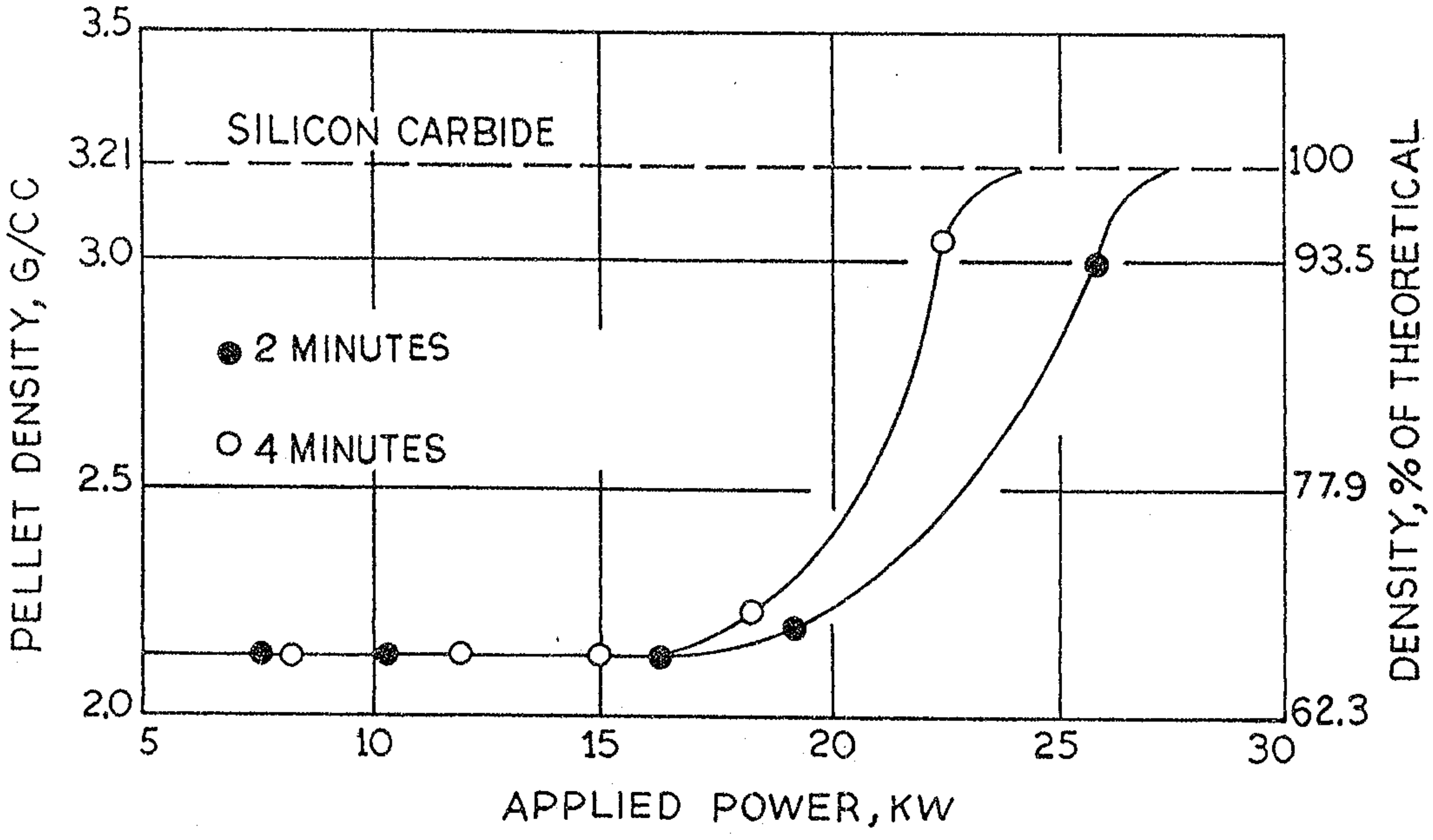


INVENTOR
WILLIAM M. GOLDBERGER

Finlayson & Singlehurst

PATENT AGENTS

Fig. 2



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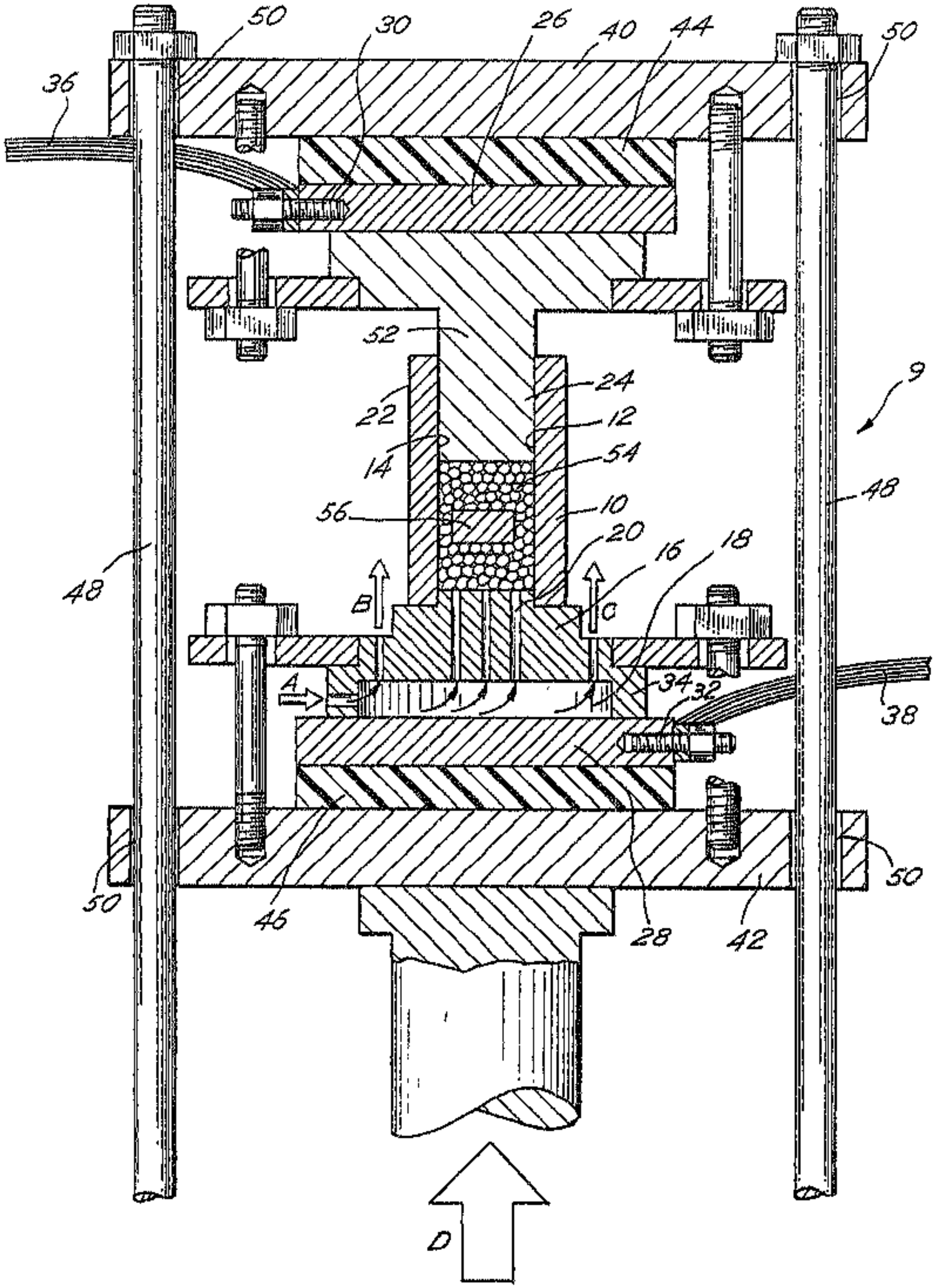

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