

[54] **APPARATUS FOR HOT PRESSING
OXIDE CERAMICS IN A CONTROLLED
OXYGEN ATMOSPHERE**

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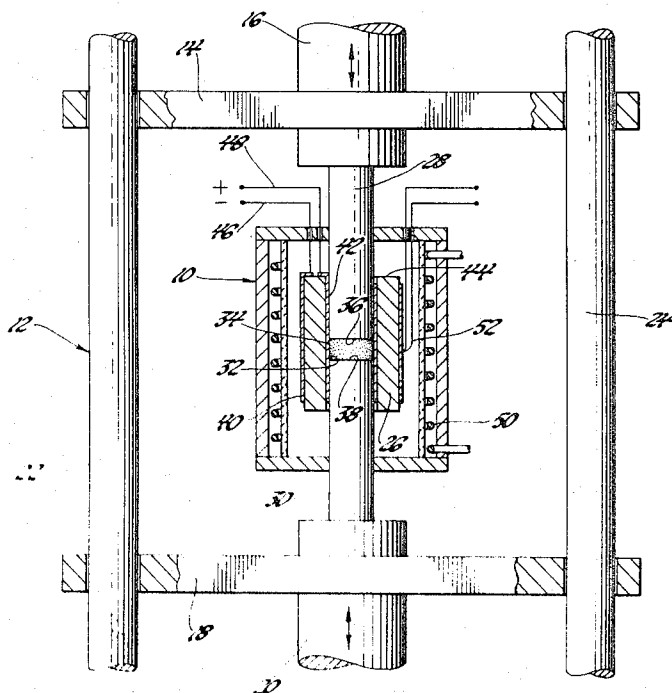
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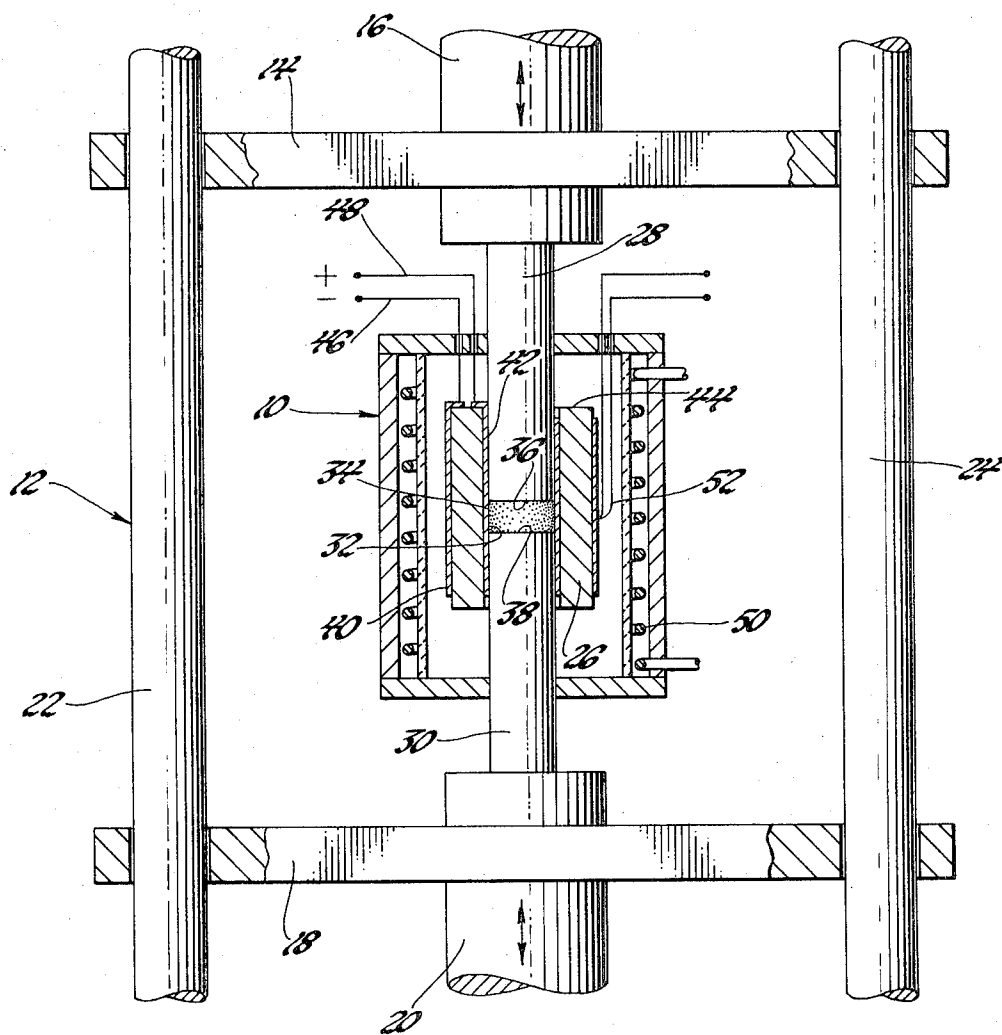
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[57] **ABSTRACT**

An improved hot press apparatus for compacting oxide ceramic powders including an electrolyte die member of a solid material conductive of oxygen ions with negligible electronic conductivity, a pair of porous electrodes applied to the inner and outer surfaces of the electrolyte die member, and a resistance heater for bringing the die member to hot press temperature is disclosed. Application of a potential to the electrodes develops a voltage across the electrolyte die member whereby oxygen molecules at the outer surface are adsorbed into the electrolyte die member, pass therethrough as oxygen ions, and are desorbed at the inner surface thereof to provide an oxygen atmosphere in the area where pressure is being applied to the oxide ceramic powder. By varying the potential applied to the electrodes the oxygen partial pressure in the die can be controlled to produce sintered oxide ceramics having improved electrical, magnetic and mechanical properties.

6 Claims, 1 Drawing Figure





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APPARATUS FOR HOT PRESSING OXIDE CERAMICS IN A CONTROLLED OXYGEN ATMOSPHERE

This invention relates to an apparatus for hot pressing oxide ceramic powders and, more specifically, to a hot press apparatus including means for controlling the oxygen partial pressure within the hot press die. As used herein the term "oxide ceramic powder" includes ferromagnetic and ferrimagnetic materials, ferroelectrics, dielectrics, piezoelectrics, resistive semiconductive, and electro-optic materials.

Of the various forming methods known to the art for fabricating formed oxide ceramic bodies from powders, e.g., cold pressing and sintering; hot pressing has been shown to have numerous advantages both in processing and in the resulting physical, electrical, and magnetic properties of the formed bodies. Hot pressing is a technique for densification of powder compacts by the simultaneous application of heat and pressure. These advantages include a reduction in the time-temperature relationship required for densification over those for normal sintering, obtaining densities of at least 95 percent of theoretical and possibly 100 percent, an increase in density without an increase in the rate of grain growth, good homogeneity, low porosity, low internal stress, and improved electrical, magnetic and mechanical properties. Further, finished shapes are formed in the hot press die eliminating cutting or machining operations and sintering procedures with accompanying dangers of high shrinkage and cracking due to shrinkage.

Hot pressing has a disadvantage, however, in that the use of enclosed hot press dies and pressing temperatures between 1,000° C and 2,000° C. result in a reducing condition in the die for the oxide ceramics being pressed which results in significant deterioration of electrical, magnetic and mechanical properties. For example, in the case of anisotropic *m* structure ferrite materials such as barium, strontium, and lead ferrites this reducing condition converts some of the iron ions from the +3 valence state to the +2 valence state. Because of the nature of the *m* structure all of the iron ions should be in the +3 valence state. As a result, these ferrites when hot pressed show poor magnetic properties even though they have been magnetically oriented, have fine grain sizes and near theoretical densities. Recognition of this problem has led to several methods for controlling the atmosphere within the die in the area where pressure is being exerted on the ferrimagnetic powder. For example, one method involves making the die of a porous material such as silicon carbide, mullite, or alumina so that the interior of the die is in gaseous communication with the furnace atmosphere. Another method merely involves forcing any desired oxidizing, reducing, or natural gas into the die cavity. A further method involves mixing with the oxide ceramic powder an agent which at the temperature of the pressing operation will gasify producing the desired atmosphere. However, each of these methods have inherent disadvantages either in the difficulty in fabricating suitable dies or in contaminating the oxide ceramic powder and, therefore, have not been found to be entirely satisfactory.

Accordingly, it is among the principal objects of this invention to provide an improved hot pressing apparatus which includes means for effectively con-

trolling the oxygen partial pressure within the die to produce a desired atmosphere therein thereby overcoming the difficulties and limitations of prior apparatus.

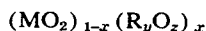
This object and others of our invention are accomplished in the preferred embodiment by providing an improved hot pressing apparatus including a tubular electrolyte die member formed of a solid material conductive of oxygen ions with negligible electronic conductivity and porous electrodes applied to both sides of the electrolyte die member with the inner electrode being the anode and the outer electrode being the cathode. Application of a potential between the electrodes develops a voltage across the electrolyte die member whereby oxygen in contact with the outer electrode is adsorbed at the electrode, diffused through the electrolyte die member as an ion and released at the anode in the mold cavity thereby raising the oxygen partial pressure in the die where physical pressure is being exerted on the oxide ceramic powder. The partial pressure of oxygen in the die is proportional to the voltage generated across the electrolyte. Accordingly, the atmosphere in the die may be effectively controlled merely by varying the potential applied to the electrodes. Further, by switching polarities, i.e., by making the inner surface cathodic and the outer anodic, oxygen can be conducted out of the die to create a reducing or neutral condition if such is desired. The apparatus also includes heating means spaced from the electrodes to heat the electrolyte die members to an elevated temperature for hot pressing of the oxide ceramic powder and for bringing the electrolyte into the region of oxygen ion conductivity.

Other objects and advantages of our invention will become more apparent from the following detailed description, reference being had to the accompanying drawing which is an elevation with parts in section of a hot press apparatus illustrative of our invention.

Referring to the accompanying drawing, there is shown a typical hot press apparatus comprising a tubular furnace 10 vertically positioned within a press frame 12 including a moving top platen 14 supported by a hydraulic piston 16 and a moving bottom platen 18 supported by a hydraulic piston 20 held in vertical alignment by support rods 22 and 24, and a tubular electrolyte die member 26 vertically positioned within the furnace 10. Slidably operative in the electrolyte die member 26 are top and bottom cylindrical punches 28 and 30, respectively, attached to the platens 14 and 18, respectively, which serve to define a mold cavity 32 therebetween which is filled with a predetermined quantity of oxide ceramic powder 34 and further to compress the oxide ceramic powder 34 into a shaped body between the ends 36 and 38 of the respective two punches. The top and bottom punches 28 and 30 are capable of automatically generating and holding a pre-set pressure by means of the hydraulic pistons 16 and 20. The oxide ceramic 34 within the mold cavity 32 may be in the form of either a powder or a preformed "green" compact. The apparatus described thus provides a double-acting hot press apparatus although it is to be understood that single acting presses are equally applicable.

The tubular electrolyte die member 26 is formed of a material conductive of oxygen ions with negligible elec-

tronic conductivity. Such materials are known to the art and are solid solutions of oxides whose compositions may be described by the general formula:



where M represents at least one tetravalent element from the group consisting of zirconium, hafnium and thorium, R represents at least one element from the group consisting of calcium, yttrium, magnesium, dysprosium, ytterbium and cerium which form cations with stable +2 and +3 valences in the oxide, x represents a number having a value of from about 0.1 to about 0.3, and y and z represent numbers having values sufficient to make R_yO_z electrically neutral. A suitable material from this group is stabilized zirconia which is a solid solution of a major portion of zirconium oxide (ZrO_2) stabilized by a minor portion of calcium oxide (CaO) and which has the ability to conduct oxygen ions by virtue of anion vacancies in the crystal lattice. The pressure-exerting punches 28 and 30 may be conveniently formed of the same material.

Disposed as a layer on the outer cylindrical surface of the tubular electrolyte die member 26 in electronically conductive contact therewith is a first electrode 40 (thickness greatly exaggerated). A second electronically conductive electrode 42 (also exaggerated) is disposed as a layer on the inner cylindrical surface of the electrolyte die member 26 directly opposing the first electrode 40. The length of the electrodes is greater than that of the mold cavity 32. The first and second electrodes 40 and 42, respectively, are in intimate contact with the electrolyte die member 26 and have electrical continuity but are sufficiently porous to permit the oxygen ions to pass through, to and out of the electrolyte die member 26. The electrode materials are formed of a material operative at the elevated temperatures of the hot pressing operation such as the platinum group metals. In the preferred embodiment, a platinum paste is used which is painted on the electrolyte die member and fired in place.

The electrodes 40 and 42 extend in part to the top surface 44 of the electrolyte die member 26 where lead conductors 46 and 48 are attached in conductive contact therewith. The lead conductors are attached to a source of potential to thereby develop a voltage across the electrolyte die member 26 between the first and second electrodes 40 and 42, respectively. For conducting oxygen ions into the mold cavity 32 the inner electrode 42 is made anodic and the outer electrode 40 is made cathodic. For conducting oxygen ions out of the mold cavity 32 the polarity is reversed.

Disposed about the electrolyte die member 26 and in spaced relation to the electrodes is a resistance heater 50 for bringing the electrolyte die member 26 to the hot press temperature, for example, to a temperature from about 500° C. to about 1,700° C. but preferably between about 1,000° and 1,200° C. The resistance heater 50 is suitably mounted in the wall of the furnace 10 which can be made of a heat-resistant material such as aluminum oxide. The high temperatures involved in the hot press operation also appreciably increase the ionic conductivity of the electrolyte 26.

Temperatures are measured by a thermocouple 52, e.g., a Pt-Pt10Rh thermocouple, which extends into the electrolyte die member 26 in close proximity to the

mold cavity 32. The thermocouple 52 can also be used for controlling automatically the power supplied to the resistance heater 50.

In operation, the bottom punch 30 is introduced into the tubular electrolyte die member 26 which is in a vertical position. A measured quantity of oxide ceramic powder 34 is introduced on the top end 38 of the punch 30. Then the top punch 28 is lowered into position. Power is then applied to the resistance heater 50 which brings the electrolyte die member 26 to the desired hot pressing temperature. A potential is also applied to the electrodes 40 and 42 to conduct oxygen into the mold cavity 32. When the hot press temperature is reached, a pre-set pressure is imposed on the powder between the ends 36 and 38 of the punches 28 and 30 for a predetermined time to compact the powder into a high density article having a shape corresponding to that of the mold cavity after which power to the resistance heater 50 is turned off and the die 26 is allowed to cool. The top punch 28 is then removed and the bottom punch 30 moved upwards to eject the formed shape from the apparatus.

During the hot press operation the outer surface of the electrolyte die member and the outer electrode 40 are exposed to the atmosphere which, of course, contains a known quantity of oxygen. An oxygen molecule from the air is adsorbed at the outer electrode 40 (or cathode), dissociates and acquires four electrons, and enters the electrolyte die member as two O^{2-} ions. The voltage between the electrodes drives the O^{2-} ions through the heated electrolyte to the inner electrode 42 (or anode) where they are desorbed, give up four electrons, and associate to form an O_2 molecule in the mold cavity thus increasing the oxygen partial pressure within the mold cavity 32. The partial pressure in the die is proportional to the voltage generated across the electrolyte die member 26, and, accordingly the oxygen atmosphere within the die can be controlled by varying the potential applied to the electrodes 40 and 42. In like manner, a reducing or neutral atmosphere can be provided, if desired, by switching polarities thus driving oxygen out of the die cavity.

Having described the preferred embodiment of our invention, the following specific examples will further serve to illustrate the efficacy of our invention.

A hot press apparatus was constructed having a tubular electrolyte die member of $\frac{3}{4}$ inch in inside diameter formed of stabilized zirconia supplied by the Zirconium Company of America. A platinum paste, No. 6926, supplied by the Engelhard Company, was used for the electrodes. To pass oxygen through the electrolyte die member a direct current of 0.5 amperes was used beginning at about 700° C. Hot press temperatures ranged from 1,000° C. to 1,200° C. Pressures varied from 2,000 psi to 6,000 psi, and press time at temperature from 10 minutes to 16 hours. The volume of the mold cavity ranged from 2cc to 7cc depending on the size of the sample. According to Faraday's law, 7.8×10^{-5} moles/minute of oxygen was passed through the electrolyte die member. Using the ideal gas law and assuming 1 atmosphere of pressure and a temperature of 1,000° C., this amounted to a flow rate of 8.2cc/minute of oxygen.

EXAMPLE I

Samples of Fe_3O_4 were hot pressed with and without oxygen flow through the electrolyte. No oxygen flow was accomplished merely by not applying a potential to the electrodes. The samples were pressed at a temperature of $1,100^\circ\text{C}$. and a pressure of 4,000 psi for 10 minutes. Fe_3O_4 has low resistivity at room temperature and is ferromagnetic. Fe_3O_4 converts to Fe_2O_3 in an oxygen atmosphere at $1,100^\circ\text{C}$. Fe_2O_3 has a high resistivity and is not ferromagnetic. Without oxygen flow through the electrolyte die member a ferromagnetic hot press product having a resistivity of 8 ohm-cm resulted. However, with oxygen flow, a non-ferromagnetic product with a resistivity of 10^{13} ohm-cm resulted indicating that the oxygen partial pressure in the mold cavity was sufficient to convert Fe_3O_4 to Fe_2O_3 .

EXAMPLE II

A barium ferrite ($\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$) material was hot pressed at a temperature of $1,150^\circ\text{C}$. and a pressure of 4,000 psi for 10 minutes. With no oxygen flow the hot pressed material had a magnetic induction (Br) of 1,800 gauss and a coercive force (Hc) of 500 oersteds. However, with oxygen flow the magnetic properties were markedly improved to a Br of 3,200 gauss and an Hc of 2,700 oersteds.

As discussed above, Fe^{+2} is detrimental to the magnetic properties of barium ferrite and results from the reduction of Fe_2O_3 to FeO within the hot press die. Chemical analysis of the barium ferrite material hot pressed with no oxygen flow showed the percent Fe^{+2} at 1.02 percent. However, with oxygen flow, the percent Fe^{+2} was 0.22 percent. Accordingly, it may be seen that the hot press apparatus embodying our invention was effective in markedly lowering the reduction of Fe^{+3} to Fe^{+2} and that higher oxygen flow rates would eliminate this reduction completely.

EXAMPLE III

To illustrate the effect of the atmosphere within the mold cavity during hot pressing on mechanical properties of ferroelectrics, it is known that oxygen has an effect on the fired density of lead-titanate-zirconate. Samples of lead-titanate-zirconate (supplied by Clevite Corp. under the tradename PZT) were hot pressed at $1,100^\circ\text{C}$. and 2,000 psi for 1 hour. With no oxygen flow the fired density was 6.87 grams/cc. However, with oxygen flow the density was increased to 7.97 grams/cc.

Although our invention has been described in terms of certain specific embodiments it is to be understood that other forms may be adopted within the skill of the art. For example, those skilled in the art will recognize that our invention is not limited to any specific die configuration or to any specific hot press apparatus.

We claim:

1. An apparatus for hot pressing oxide ceramic powders in the presence of a controlled oxygen atmosphere comprising, an electrolyte die member of a solid material conductive of oxygen ions with negligible electronic conductivity having inner and outer surfaces and having a mold cavity therein adapted to contain oxide ceramic powder, a first electrode contacting the outer surface of said electrolyte die member, a second electrode

contacting the inner surface of said electrolyte die member, first and second conductors contacting said first electrode and said second electrode, respectively, for applying a potential between said first and said second electrodes to develop a voltage across said electrolyte die member, means for heating said die member to an elevated temperature, and means for applying pressure to said die member to mold said oxide ceramic powder while said potential between said first and second electrodes is applied and while said die member is heated to said elevated temperature.

2. An apparatus for hot pressing oxide ceramic powders in the presence of a controlled oxygen atmosphere comprising, an electrolyte die member of a solid material conductive of oxygen ions with negligible electronic conductivity having inner and outer surfaces and having a mold cavity therein adapted to contain oxide ceramic powder, a first electrode contacting the outer surface of said electrolyte die member, a second electrode contacting the inner surface of said electrolyte die member, first and second conductors contacting said first electrode and said second electrode, respectively, for applying a potential between said first and said second electrodes to develop a voltage across said electrolyte die member, said first electrode being the cathode and said second electrode being the anode, means for heating said die member to an elevated temperature, and means for applying pressure to said die member to mold said oxide ceramic powder while said potential between said first and second electrodes is applied and while said die member is heated to said elevated temperature.

3. An apparatus for hot pressing oxide ceramic powders in the presence of a controlled oxygen atmosphere comprising, a tubular electrolyte die member of a solid material conductive of oxygen ions with negligible electronic conductivity having inner and outer cylindrical surfaces, a pair of opposed cylindrical punches slidably movable within said tubular electrolyte die member defining a closed mold cavity therebetween adapted to contain oxide ceramic powder, a first electrode contacting the outer surface of said electrolyte die member, a second electrode contacting the inner surface of said electrolyte die member, first and second conductors contacting said first electrode and said second electrode, respectively, for applying a potential between said first and said second electrodes to develop a voltage across said electrolyte die member, and means for heating said die member to an elevated temperature, said opposed cylindrical punches being operative to apply pressure to mold said oxide ceramic powder while said potential between said first and second electrodes is applied and while said die member is heated to said elevated temperature.

4. An apparatus for hot pressing oxide ceramic powders in the presence of a controlled oxygen atmosphere comprising, a tubular electrolyte die member of a solid material conductive of oxygen ions with negligible electronic conductivity having inner and outer cylindrical surfaces, a pair of opposed cylindrical punches slidably movable within said tubular electrolyte die member defining a closed mold cavity therebetween, adapted to contain oxide ceramic powder, a first electrode disposed as a layer in direct contact with the outer surface of said electrolyte die member, a second electrode

disposed as a layer in direct contact with the inner surface of said electrolyte die member, said first and second electrode layers having a substantial portion of their surfaces directly opposing each other and having a length greater than said mold cavity, first and second conductors contacting said first electrode and said second electrode, respectively, for applying a potential between said first and said second electrodes to develop a voltage across said electrolyte die member, and means for heating said die member to an elevated temperature, said opposed cylindrical punches being operative to apply pressure to mold said oxide ceramic powder while said potential between said first and second electrodes is applied and while said die member is heated to said elevated temperature.

5. An apparatus for hot pressing oxide ceramic powders in the presence of a controlled oxygen atmosphere comprising, a tubular electrolyte die member of a solid material conductive of oxygen ions with negligible electronic conductivity having inner and outer cylindrical surfaces, a pair of opposed cylindrical punches slidably movable within said tubular electrolyte die member defining a closed mold cavity therebetween adapted to contain oxide ceramic powder, a first porous, electronically conductive electrode disposed as a layer in direct contact with the outer surface of said electrolyte die

member, a second porous, electronically conductive electrode disposed as a layer in direct contact with the inner surface of said electrolyte die member, said first and second electrode layers having a substantial portion of their surfaces directly opposing each other and having a length greater than said mold cavity, first and second conductors contacting said first electrode and said second electrode, respectively, for applying a potential between said first and said second electrodes to develop a voltage across said electrolyte die member, and means in spaced relation to said electrolyte die member for heating said die member to an elevated temperature, said opposed cylindrical punches being operative to apply pressure to mold said oxide ceramic powder while said potential between said first and second electrodes is applied and while said die member is heated to said elevated temperature.

6. The apparatus as defined in claim 5 wherein said electrolyte die member consists essentially of a major portion of zirconium oxide stabilized with a minor portion of calcium oxide, said electrodes consist essentially of platinum, and said heating means is operative to heat said die member to a temperature between about 500° C. and 1,700° C.

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