The present invention provides a production method for a sintered metal-ceramic layered compact, comprising steps of: filling and layering a metal powder and a ceramic powder, or filling and layering a metal powder, a mixed powder of a metal powder and a ceramic powder, and a ceramic powder; forming a green compact of the layered powders by compacting the layered powders; and sintering a layer including the metal of the green compact at a temperature of lower than a melting point of the metal by heating by irradiation of microwaves in a non-oxidizing atmosphere.
Fig. 3

Fig. 4
Fig. 5A

310a

Fig. 5B

310b

Fig. 5C

310c

Fig. 5D

310d
Fig. 9A

Fig. 9B

Fig. 9C
PRODUCTION METHOD FOR SINTERED METAL-CERAMIC LAYERED COMPACT AND PRODUCTION METHOD FOR THERMAL STRESS RELIEF PAD

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a production method for producing metal-ceramic layered compacts by using a powder metallurgy technique, and relates to a production method for producing thermal stress relief pads for thermoelectric conversion elements by using a powder metallurgy technique. The metal-ceramic layered compact is heat resistant and thermally conductive, or is electrically insulated at one portion thereof and electrically conductive and thermally conductive at another portion thereof, and has a required thermal stress relief function. The thermal stress relief pad has a structure in which metal and ceramic are layered and which is electrically conductive and electrically insulated.

2. Description of the Related Art

A metal-ceramic layered compact which is heat resistant and heat dissipating is disclosed in, for example, Japanese Unexamined Patent Application Publication No. 5-286776, as described below. That is, a metal-ceramic layered compact has an intermediate layer between a metal layer and a ceramic layer. The metal layer is made of copper, nickel, or tungsten. The ceramic layer is made of alumina, aluminum nitride, or boron nitride. The intermediate layer is made of metal and ceramic such that the mixing ratio of metal and ceramic varies gradually or continuously in a thickness direction. This layered compact is produced as follows. That is, a metal included layer is layered by thermal spraying on a ceramic substrate or is layered by paste printing thereon, and is then sintered by hot pressing, by hot isostatic pressing (HIP), or by an electrosputtering heating method in which voltage is directly applied thereto so that plasma discharge is generated among grains thereof.

A metal-ceramic layered compact is disclosed in, for example, Japanese Unexamined Patent Application Publication No. 6-329480, as described below. The metal-ceramic layered compact has an intermediate layer between an alumina substrate and a copper plate. The intermediate layer is composed of tungsten, silver-copper alloy, and titanium. The composition of the intermediate layer is set such that the silver-copper alloy is included more on the copper plate side. The intermediate layer is laminated by paste printing, and is then sintered in a vacuum or in an atmosphere of nitrogen gas, hydrogen gas, or argon gas.

In the above conventional techniques, the metal-ceramic layered compact is obtained such that metal layers are layered by thermal spraying or by paste printing on a presintered ceramic substrate, and the metal layers are then sintered. The ceramic has high strength and the metal-ceramic layered compact has good thermal conductivity since the metal layers have fine structures. However, in the above production methods, after the ceramic is sintered at high temperatures, the following processes are repeatedly performed. That is, a thermal spraying process is sequentially performed on metal containing powders which have different compositions from each other, or pasted materials are printed, and a drying process is performed. Due to this, the above techniques require numerous processes, are time consuming, and are troublesome. As a result, it is desired that a metal-ceramic layered compact be more easily produced.

A thermal stress relief pad for a thermoelectric conversion element is disclosed in, for example, Japanese Unexamined Patent Application Publication No. 10-229224 as described below. That is, the thermal stress relief pad has an electrical insulating layer made of ceramic at the intermediate portion in a thickness direction, and metal layers are formed via a mixed layer of ceramic (electrical insulating material) and metal (thermoelectric stress relief material and thermal conductivity compact) on both sides of the electrical insulating layer. In this case, the mixed layer is a graded function layer having a gradient component in which the ceramic is included more on the electrical insulating layer and the metal is included more on the metal layer. This thermal stress relief pad is used such that one end face thereof is contacted to an electrode side of the thermoelectric element and the other end face is contacted to a side of a heat source or to a side of a cooling device. As a result, thermal stress relief pad has good thermal conductivity, is prevented from leaking electricity to the heat source side or to the cooling device by the electrical insulating layer, and yields a thermal stress relief function by having the graded composition in a thickness direction. For example, the mixture of the electrical insulating material and the metal is composed of alumina and copper, and is produced such that powder filling is performed by injecting each powder from a nozzle into a die while controlling the injecting ratio thereof so as to have a graded composition in a thickness direction, and then compacting and sintering are performed on the layered powders in the die.

In the production method disclosed in the Japanese Unexamined Patent Application Publication No. 10-229224, when a multilayered structure having a graded composition layer is produced, a method as described below can be used instead of the multilayered filling method by the above powder spraying. That is, one or more kinds of a mixed powder and a metal powder are layered, are filled by using a powder feeder, and are formed by compacting in turn in a die. The mixed powder is composed of an electrical insulating powder (for example, alumina powder) and a metal powder (for example, copper powder). However, since a thermal stress relief pad for thermoelectric conversion elements generally has a structure such that a conductive metal-ceramic mixed layer and a metal layer are formed on both sides of the electrical insulating layer (for example, alumina simple substance) which is at a middle portion in a thickness direction thereof, when the powders are sequentially filled and layered, the metal powder enters an outer face of the electrical insulating layer via an inner wall surface of the die. In this case, metal foil is formed on the outer face of the electrical insulating layer, and causes a short circuit in the thermal stress relief pad.

In addition, in the production method disclosed in Japanese Unexamined Patent Application Publication No. 10-229224, a green compact has a structure such that the electrical insulating layer made of, for example, alumina powder, and is disposed between the mixed powder of alumina and copper. However, since this green compact is sintered at a temperature at which copper does not melt, an
alumina compact of the electrical insulating layer is not sintered well, and cracks thereby occur at the electrical insulating layer portion. As a result, the sintered compact requires care in the use thereof.

**SUMMARY OF THE INVENTION**

**[0010]** An object of the present invention according to an aspect of the invention is to provide a production method for a sintered metal-ceramic layered compact, which can reduce the number of processes and can be performed efficiently.

**[0011]** An object of the present invention according to another aspect of the invention is to provide a production method for thermal stress relief pads for thermoelectric conversion elements, in which, however, compacting is performed on the powders by using a die, can prevent a short circuit which is caused by metal materials and can yield reliable performance of an electrical insulating layer.

**[0012]** An object of the present invention according to another aspect of the invention is to provide a production method for thermal stress relief pads for thermoelectric conversion elements, which can reduce the number of processes and can be performed efficiently.

**[0013]** The present invention provides a production method for a sintered metal-ceramic layered compact, comprising steps of: filling and layering a metal powder and a ceramic powder, or filling and layering a metal powder, a mixed powder of a metal powder and a ceramic powder, and a ceramic powder; forming a green compact of the layered powders by compacting the layered powders; and sintering a layer including the metal of the green compact at a temperature of lower than a melting point of the metal by heating by irradiation of microwaves in a non-oxidizing atmosphere.

**[0014]** The present invention further provides a production method for a sintered metal-ceramic layered compact, comprising steps of: filling and layering a metal powder and a ceramic powder, or filling and layering a metal powder, a mixed powder of a metal powder and a ceramic powder, and a ceramic powder; forming a green compact of the layered powders by compacting the layered powders; presintering a layer including the metal of the green compact at a temperature lower than a melting point of the metal by heating by irradiation of microwaves in a non-oxidizing atmosphere; and sintering the presintered compact at a temperature lower than a melting point of the metal in a non-oxidizing atmosphere.

**[0015]** According to the present invention, the step of compacting the powders and the step of sintering the green compact by using powder metallurgy are performed when the sintered metal-ceramic layered compact is produced. As a result, the number of processes can be reduced and the production is performed efficiently.

**[0016]** The production method can use a microwave heating furnace provided with a cooling device, and a side of the metal layer of the compact may be contacted to the cooling device of the microwave heating furnace in the step of sintering the green compact.

**[0017]** In the production method of the present invention, the metal may be selected from a group consisting of copper, aluminum, silver, and nickel, or a mixture thereof, and the ceramic may be alumina or aluminum nitride.

**[0018]** In the present invention, the following embodiments can be used. The ceramic powder may include at least one low melting point powder selected from a group consisting of boric acid, anhydrous borax, sodium triboride, sodium pentaboride, and soda-lime glass, and the low melting point powder may be mixed in a ratio of not more than 50 mass % in the ceramic powder. The ceramic powder may include at least one binder selected from a group consisting of methyl cellulose (MC), polyvinyl alcohol (PVA), ammonium alginate, carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), and polyvinyl pyrrolidone (PVP), and the binder may be mixed in a ratio of not more than 1 mass % in the ceramic powder. The mixed powder of the ceramic powder and the binder may be granulated to have a particle diameter of not more than 150 μm. The mixed powder of the metal powder and the ceramic powder may have two or more mixed powders which have different compositions from each other, wherein the metal may be mixed in a volume not less than that of the ceramic powder in the mixed powder disposed on the side of the metal layer, and the ceramic powder may be mixed in a volume not less than that of the metal powder in the mixed powder disposed on the side of the ceramic layer.

**[0019]** The present invention further provides a production method for a sintered metal-ceramic layered compact, comprising steps of: filling and layering a metal powder and a ceramic powder, or filling and layering a metal powder, a mixed powder of a metal powder and a ceramic powder, and a ceramic powder; forming a green compact of the layered powders by compacting the layered powders; and sintering the green compact at a temperature lower than a melting point of the metal in a non-oxidizing atmosphere.

**[0020]** According to the present invention, the step of compacting the powders and the step of sintering the green compact by using powder metallurgy are performed when the sintered metal-ceramic layered compact is produced. As a result, the number of processes can be reduced and the production is performed efficiently.

**[0021]** The present invention further provides a production method for a thermal stress relief pad for thermoelectric conversion elements, comprising steps of: filling and layering an electrical insulating powder (30C) and a mixed powder (30B) of a metal powder and an electrical insulating powder in turn in a cavity of a die, and forming a green compact (31) of the layered powders by compacting the layered powders, or filling and layering an electrical insulating powder (30C), a mixed powder (30B) of a metal powder and an electrical insulating powder, and a metal powder (30A) in turn in a cavity of a die, and forming a green compact (32) of the layered powders by compacting the layered powders; and contacting an electrical insulating layer, which is made of the electrical insulating powder (30C) in either the green compact (31) or the green compact (32), to a surface of an electrical insulating layer of the electrical insulating powder (30C) in either the green compact (31) or the green compact (32); or filling a mixed powder (30B) of a metal powder and an electrical insulating powder in a cavity of a die, and forming a green compact (33) by compacting the powder, and contacting an electrical insulating layer, which is made of the electrical insulating...
powder (30C) in either the green compact (31) or the green compact (32), to a surface of the green compact (33), or filling and layering a metal powder (30A) and a mixed powder (30B) of a metal powder and an electrical insulating powder in turn in a cavity of a die, and forming a green compact (34) of the layered powders by compacting the layered powders, and contacting an electrical insulating layer, which is made of the electrical insulating powder (30C) in either the green compact (31) or the green compact (32), to a surface of the green compact (34), and sintering the green compacts, which are in the above contacting state to each other, at a temperature lower than a melting point of the included metal in a non-oxidizing atmosphere.

[0022] According to the present invention, the metal powder, the mixed powder of the metal powder and the electrical insulating powder, and the electrical insulating powder are filled and layered in an appropriate multilayered structure, two green compacts are thereby obtained, are appropriately combined with each other, and then are sintered at a temperature lower than the melting point of the included metal in a non-oxidizing atmosphere. As a result, short-circuiting caused by metal materials can be prevented and the electrical insulating layer can function reliably although compacting is performed on the powders by using the die in the production method of the present invention.

[0023] The present invention further provides a production method for a thermal stress relief pad for thermoelectric conversion elements, comprising steps of filling and layering a mixed powder (30B) of a metal powder and an electrical insulating powder, an electrical insulating powder (30C), and a mixed powder (30B) of a metal powder and an electrical insulating powder in turn in a cavity of a die, or filling and layering a metal powder (30A), a mixed powder (30B) of a metal powder and an electrical insulating powder, an electrical insulating powder (30C), a mixed powder (30B) of a metal powder and an electrical insulating powder, and a metal powder (30A) in turn in a cavity of a die; forming a green compact of the layered powders by compacting the layered powders; sintering the green compact at a temperature lower than a melting point of the included metal powder in a non-oxidizing atmosphere; and removing a side surface portion of the sintered compact by cutting or by polishing.

[0024] In the present invention, the electrical insulating powder may be a mixed powder (30C1), a mixed powder (30C2), or a glass frit powder (30C3), wherein the mixed powder (30C1) may be composed of one of an alumina powder and an aluminum nitride powder, and one low melting point electrical insulating powder selected from a group consisting of boric acid, sodium borate, and soda-lime glass, the low melting point electrical insulating powder being mixed in a ratio of not more than 50 mass %; the mixed powder (30C2) may be composed of one of an alumina powder and an aluminum nitride powder and a glass frit which is mixed in a ratio of not less than 0.1 mass %, and the metal powder (30A) may be selected from a group consisting copper, aluminum, silver, and nickel, or a mixture thereof.

[0025] The present invention further provides a production method for a thermal stress relief pad for thermoelectric conversion elements, comprising steps of: filling and layering an electrical insulating material powder (40A) for an electrical insulating material layer and a mixed powder (40B) of a metal powder and an electrical insulating material powder in a die, or filling and layering an electrical insulating material powder (40A) for an electrical insulating layer, a mixed powder (40B) of a metal powder and an electrical insulating material powder, and a metal powder (40C) in a die; forming a green compact of the layered powders by compacting the layered powders; and sintering the green compact at a temperature lower than a melting point of the included metal powder in a non-oxidizing atmosphere, wherein the metal powder is selected from a group consisting of copper, aluminum, silver and nickel, or a mixture thereof, the electrical insulating material powder (40A) is selected from a group consisting of a glass frit (40A1) and a mixed powder (40A2) of a ceramic powder and a glass frit, the ceramic powder being composed of alumina or aluminum nitride, the electrical insulating material powder (40A) included in the mixed powder (40B1) is selected from a group consisting of a ceramic powder, the glass frit (40A1), and a mixed powder (40A2) of a ceramic powder and a glass frit.

[0026] According to the present invention, the step of compacting the powders and the step of sintering the green compact by using powder metallurgy are performed when the sintered metal-ceramic layered compact is produced. As a result, since the electrical insulating layer and the metal layer can be sintered simultaneously when the thermal stress relief pad for thermoelectric conversion elements is produced, the number of processes can be reduced and the production is performed efficiently.

[0027] In the present invention, the electrical insulating material powder (40A) may be a mixed powder (40A2) of the ceramic powder and the glass frit, and the glass frit may be mixed in a ratio of not less than 0.1 mass % in the mixed powder (40A2). The following concrete methods can be used in the present invention. That is, the mixed powder (40B1), the electrical insulating material powder (40A) and the mixed powder (40B2) may be layered in turn in the die in the step of filling and layering powders, or the metal powder (40C), the mixed powder (40B1), the electrical insulating material powder (40A), the mixed powder (40B2), and the metal powder (40C) may be layered in turn in the die in the step of filling and layering powders, and the layered powders may be integrally compacted in the step of compacting. Alternatively, the mixed powder (40B1) and the electrical insulating material powder (40A) may be layered in turn in the die in the step of filling and layering powders, or the metal powder (40C), the mixed powder (40B1) and the electrical insulating material powder (40A) may be layered in turn in the die in the step of filling and layering powders, the layered powders are integrally compacted in the step of compacting, whereby two green compacts are obtained, and the green compacts may be sintered in a state in which surfaces of layers of the electrical insulating material powder (40A) are contacted to each other in the sintering step, thereby being connected.

[0028] The following concrete methods can be used in the present invention. That is, the electrical insulating material powder (40A) may include at least one binder selected from a group consisting of methyl cellulose (MC), polyvinyl alcohol (PVA), ammonium alginate acid, carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), and polyvinyl pyrrolidone (PVP), wherein the binder may be mixed in a ratio of not more than 1 mass %. The binder may be mixed
into the electrical insulating material powder (40A) in a middle portion layer in a thickness direction, and the mixed powder may be granulated so as to have a particle diameter of not more than 150 μm.

[0029] The present invention further provides a production method for a thermal stress relief pad for thermoelectric conversion elements, comprising steps of: filling a mixed powder (40B) of a metal powder and an electrical insulating material powder in a die, or filling and layering a mixed powder (40B) of a metal powder and an electrical insulating material powder, and a metal powder (40C) in turn in a die; forming a green compact of the layered powders by compacting the layered powders, whereby two green compacts of the layered powders are obtained; coating an electrical insulating material powder (40A) on a surface of a layer of the mixed powder (40B) of one of the green compacts; and connecting the green compacts via the electrical insulating material powder (40A) by sintering. In this case, the electrical insulating material powder (40A) coated on a surface of a layer of the mixed powder (40B) may be dispersed in a liquid so as to be made into slurry.

[0030] In the both methods of the present invention, the mixed powder (40B) can have two or more mixed powders which have different composition from each other, the metal powder (40C) can be mixed in a volume not less than that of the electrical insulating material powder (40A) on the side of the metal layer formed on an end face, and the electrical insulating material powder (40A) can be mixed in a volume more than that of the metal powder (40C) in an electrical insulating layer formed at a middle portion in a thickness direction.

BRIEF DESCRIPTION OF THE DRAWINGS

[0031] FIGS. 1A to 1E are cross sectional views showing examples of a multilayered structure of a sintered ceramic-metal layered compact according to the first and the second embodiments.

[0032] FIGS. 2A and 2B are cross sectional views showing examples of a sintered ceramic-metal layered compact applied to a thermoelectric conversion module according to the first and the second embodiments.

[0033] FIG. 3 is a cross sectional view showing an example of a multilayered structure of a thermal stress relief pad according to the third embodiment.

[0034] FIG. 4 is a cross sectional view for explaining that a copper foil portion causing a short-circuit is formed at an electrical insulating layer of a sintered compact obtained by integrally compacting all powders.

[0035] FIGS. 5A to 5D are cross sectional views showing examples of a compressed material.

[0036] FIGS. 6A to 6G are cross sectional views showing examples of a thermal stress relief pad.

[0037] FIG. 7 is a cross sectional view showing an example of a thermal stress relief pad applied to a thermoelectric conversion module according to the third embodiment.

[0038] FIGS. 8A to 8C are cross sectional views showing examples of a multilayered structure for thermal stress relief pads according to the fourth embodiment.

[0039] FIGS. 9A to 9C are cross sectional views showing examples of a thermal stress relief pad.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0040] Preferred embodiments of the present invention will be described hereinafter with reference to the Figures.

[0041] (A) First Embodiment

[0042] Desirable materials and production method in which the desirable materials are used according to the first embodiment will be described in detail hereinafter.

[0043] (1) Ceramic Powder

[0044] A Ceramic powder is composed of alumina or aluminum nitride, which has good electrical insulation and good thermal conductivity. In this case, in particular, alumina has better powder compression compactability than that of aluminum nitride, and has a lower melting point than that of aluminum nitride, thereby being favorably used. A ceramic powder as a component of a ceramic layer is favorably densified as high as possible by compacting, and has good sinterability, thereby favorably having fine grain size. When a ceramic powder has low flowability due to fine grain size thereof, the ceramic powder is favorably granulated by using a binder such as carboxymethyl cellulose (CMC) so as to have a particle diameter of about 50 to 150 μm, and the flowability thereof is thereby improved. As a result, powder filling into a die is easily performed and the ceramic powder compact has high strength. As compared with a fine ceramic powder, a coarse powder is mixed with the fine ceramic powder, and the sinterability and flowability can thereby be improved. A ceramic powder which is mixed with a mixture of metal and ceramic and which is component of an intermediate layer favorably has the grain size approximate to that of the metal powder so that the ceramic powder is equally dispersed in the metal powder and the metal powder is sintered.

[0045] (2) Low Melting Powder Added to Ceramic Powder

[0046] A ceramic layer of only alumina can be sintered by irradiation of microwaves. A electrical insulating material, which is softened or has a liquid phase at temperatures at which layered metal does not melt, is formed into a powder and is mixed into a ceramic layer, whereby liquid phase sintering is performed on the ceramic layer at relatively low temperatures, thereby having high strength.

[0047] This low melting point powder is as follows.

[0048] a) boric acid (H₃BO₃): melting point of 577°C in a state of anhydrous boric acid

[0049] b) anhydrous borax (Na₂B₂O₇): melting point of 741°C

[0050] c) sodium pentaboric acid (Na₂B₅O₉·5H₂O): melting point of 750°C

[0051] d) sodium triboric acid (NaB₃O₆): melting point of 694°C

[0052] e) soda-lime glass (SiO₂—Na₂O—CaO—Al₂O₃—MgO): softening point of 500 to 700°C; melting point of about 725°C.
In the low melting point powder, plural low melting point materials and high melting point materials can be added to a ceramic layer. When the adding ratio of the low melting point powder is about 0.1 mass % in the ceramic layer, the strength of the ceramic layer is improved. When the adding ratio of the low melting point powder is larger, the liquid phase of the low melting point powder may possibly bubble to the surface of the ceramic layer in the case of sintering the ceramic layer or in the case in which the temperature range of a sintered metal-ceramic layered compact is high, whereby the adding ratio of the low melting point powder is not more than 50 mass % in the ceramic layer.

(3) Binder for Ceramic Powder

A green compact of a ceramic layer has predetermined strength so as to be easily handled by adjusting the grain size distribution of a ceramic powder. A binder such as methyl cellulose (MC), polyvinyl alcohol (PVA), ammonium alginate, carboxymethyl cellulose (CMC), or polyvinyl pyrrolidone (PVP) is mixed into a ceramic layer, or is mixed into a ceramic powder for granulating, whereby the green compact can have higher strength. As a result, when the green compact is transferred in processes of powder compacting and of sintering, cracks and defects can be prevented from forming therein. Although the green compact can be produced without the above binder, it is desirable that flowability of the ceramic powder be improved by granulating the ceramic powder so that filling to a die is improved.

The above binder dissipates when heated during the sintering of the ceramic layer. Since the density of the ceramic layer is reduced and the thermal conductivity thereof is deteriorated when too much of the above binder is added much, the mixing ratio of the above binder into the ceramic layer is favorably not more than 1 mass %.

(4) Powder of Metal Layer

A metal layer which is electrically conductive and thermally conductive is made of a metal powder. The metal powder is composed of one of copper, aluminum, silver, and nickel, or mixture of at least two of copper, aluminum, silver, and nickel. For example, the mixture may be composed of copper and aluminum. Although these powders have good compressibility, these powders favorably have predetermined grain sizes so as to pass through a 100-mesh sieve, thereby facilitating filling into a die. When a fine powder is used, flowability can be improved by granulating.

(5) Powder of Intermediate Layer

An intermediate layer is made of a metal powder and a ceramic powder. The volume ratio of the metal powder to the ceramic powder is about 1:1. Alternatively, when plural intermediate layers of the metal powder and the ceramic powder are formed, the component ratio of the metal powder to the ceramic powder increases as the intermediate layers approach the metal layer, and the component ratio of the ceramic powder to the metal powder increases as the intermediate layers approach the ceramic layer. The mixed powders are made such that the ceramic powder is mixed into the metal powder without granulation so that these powders are equally dispersed.

(6) Lubricant

It is not necessary to mix a lubricant into the metal powder because the metal powder has good compressibility. A lubricant such as metal stearate is favorably coated on an inner wall of a die so that the green compact is easily ejected from the die. The lubricant is coated by electrostatic coating. Alternatively, the lubricant dispersed in a liquid is used.

(7) Multilayered Structure

A multilayered structure has a metal layer and a ceramic layer, has a metal layer, an intermediate layer and a ceramic layer, has a metal layer, an intermediate layer, a ceramic layer and an intermediate layer, or has a metal layer, an intermediate layer, a ceramic layer, an intermediate layer and a metal layer in turn on an end face of a layered direction. The intermediate layer has at least one layer. The ceramic layer has relatively low thermal conductivity, thereby being favorably thinly formed. However, when the ceramic layer is formed very thinly, the layers which are adjacent thereto and which include metal are easily mixed, and the electrical insulation may be possibly reduced. Therefore, the thickness of the ceramic layer is favorably about 0.5 to 2 mm.

(8) Multilayered Filling of Powders

A powder feeder can be used for filling each powder in a die having a die for forming an outer portion of a green compact, an upper punch and a lower punch. The powder feeder can be moved forward or backward on a die cavity. Plural powder boxes are connected to the powder feeder in a powder feeder moving direction. For example, when a multilayered structure has a metal layer, an intermediate layer, a ceramic layer, an intermediate layer and a metal layer, the powder feeder has three boxes. In this case, a metal powder is filled in the front box, an intermediate layer powder is filled in the middle box, and a ceramic powder is filled in the rear box. The powder feeder is moved forward in a state in which the lower punch is flush with the upper face of the die, so that the powder box having the metal powder is stopped on the lower punch, and then the lower punch or the die is moved so as to form a cavity, whereby the metal powder is filled therein. Next, the box having the intermediate layer powder is moved on the die cavity, and then the intermediate layer powder is filled in the same manner as that of the metal powder. After the ceramic powder is filled in the same manner as that of the metal powder, the powder feeder is moved in turn backward, and multilayered filling of five layers can be performed. A powder feeder has a structure such that spaces are provided between plural powder boxes. In this case, after one kind of powder is filled in the cavity, in a state in which the space is stopped on the cavity, the filled powder is dropped, the cavity is formed, and the filled powder adhered on the wall surface of the die cavity is scratched and dropped by using a simple punch. As a result, a green compact having a multilayered structure which is distinctively divided can be obtained.

Since surfaces of the filled powders have microscopic rough portions, the powders adjacent to each other have slightly mixed portions of each other. The intermediate layer and the ceramic layer have slightly mixed portions in the same manner. As a result, the compositions of the layers...
are not distinctively divided from each other, and the layers adjacent to each other are mixed so as to be connected to each other, and each layer is difficult to peel off from the green compact.

[0068] (9) Compacting of Powders

[0069] Compacting is performed on the metal powders of the above metal powders as described below. That is, compacting is performed on the copper powder, the silver powder, and the aluminum powder at a compacting pressure of about 100 to 300 MPa, and is performed on the nickel powder at a compacting pressure of about 400 MPa of the above metal powders, whereby the green compacts of these metal powders have the relative density of not less than 95% and thereby have good electrical conductivity and good thermal conductivity. On the other hand, when compacting is performed on the ceramic powder of alumina at a compacting pressure of about 600 MPa, the green compact of the ceramic powder of alumina has a relative density of about 50%. When compacting is performed on the ceramic powder of alumina at a compacting pressure of 700 MPa, the green compact of the ceramic powder of alumina has a relative density of about 60%. The compacting pressure of the multilayered powder is favorably about 700 to 1000 MPa since the relative density of the green compact of the ceramic powder gradually increases when compacting is performed on the ceramic powder of alumina at a compacting pressure of more than 700 MPa.

[0070] (10) Microwave Sintering

[0071] A microwave sintering furnace is used for sintering. For example, as disclosed in Japanese Unexamined Patent Application Publication No. 6-345541, a microwave sintering furnace provided with a heater at an inner wall portion of a heating chamber can control preheating and cooling, thereby being favorably used. The inside of the heating chamber contains a non-oxidizing gas or a vacuum when the green compacts are sintered. The non-oxidizing gas may be hydrogen, nitrogen, or argon, or may be a mixed gas of hydrogen and nitrogen. When the metal powder is composed of silver, sintering can be performed in air. The furnace is constructed such that a supporting pedestal and a holding plate on which a sintered compact held is are provided in the heating chamber, and heat discharging and cooling are performed thereon by a water cooling device provided apart therefrom so that the green compact can be sintered at a high temperature at which the ceramic is sintered well without melting metal of the green compact, thereby being favorable when a metal powder of aluminum having a low melting point is used.

[0072] When microwaves are irradiated on a multilayered green compact of metal and ceramic, the ceramic is heated and the temperature thereof is increased so that the degree of sintering of the ceramic is progressed. Since the metal portion of the multilayered green compact reflects microwaves, the metal portion is not significantly heated by the microwaves. However, the temperature of the metal portion is increased by Joule heat, by heat conducted from the ceramic, and/or by radiant heat, so that the degree of sintering of the metal portion is progressed. Since the shape thereof is collapsed when the intermediate layer including the metal and the metal layer is melted, the output of the microwaves and processing time thereof are appropriately determined by experience in accordance with the kind of metal and quantity of the green compact.

[0073] The lubricant and the binder are dissipated by microwave sintering, and the ceramic layer, the intermediate layer, and the metal layer are sintered. When a low melting point powder such as a soda-lime glass is included in the ceramic layer, the low melting point powder is melted without heating the ceramic layer to a high temperature, and the ceramic layer is sintered and the interface portion between the ceramic layer and the intermediate layer has high bonding strength. In particular, a method in which a low-melting point powder is added to the ceramic powder and aluminum having low melting point is used is favorable since the ceramic layer is sintered at a low temperature without melting the aluminum.

[0074] When microwave sintering is performed, the metal layer is electrically conductive and thermally conductive, and wettability is ensured when brazing or adhering by an adhesive agent is performed in using the sintered multilayered compact.

[0075] (11) Resintering

[0076] Although in the above microwave sintering, a sintered multilayered compact of metal and ceramic can be obtained, when boric acid or anhydrous borax is included in the ceramic layer, a two step sintering method can be adopted as described below. That is, microwave sintering is briefly performed on the ceramic portion, the microwave sintering is stopped so that the metal portion is incompletely sintered, and then the presintered compact is heated at a temperature at which the metal is not melted in a non-oxidizing atmosphere. This sintering can be performed in a typical continuous sintering furnace, and is thereby suitable for mass production. In the apparatus provided with the heater in the inner wall of the heating chamber as disclosed in the above Japanese Unexamined Patent Application Publication No. 6-345541, resintering can be performed on the presintered compact by heating by the heater after stopping microwave irradiation.

[0077] Next, the first embodiment of the present invention will be described with reference to the Figures.

[0078] FIGS. 1A to 1E are cross sectional diagrams showing sintered metal-ceramic layered compact. In the sintered metal-ceramic layered compacts, the metal layer is made of copper and the ceramic layer is made of alumina.

[0079] A sintered layered compact 105A shown in FIG. 1A has a two-layered structure having a copper layer 103 and a ceramic layer 101 layered on the copper layer 103. The copper layer 103 is made of an electrolytic copper powder, and the ceramic layer 101 is made of a powder in which anhydrous borax (Na₂B₄O₇) is mixed into alumina powder in a ratio of 1 mass%. In producing the sintered layered compact 105A, the above powders are filled and layered in turn at a predetermined thickness in a die, and then compacting is performed on the filled layered powders at a compacting pressure of 800 MPa, whereby a green compact is obtained. Next, this green compact is provided in the microwave sintering furnace, nitrogen gas is charged therein, and microwaves are irradiated on the green compact so that the ceramic layer 101 is heated for five minutes at a temperature of about 900°C. and is then cooled. The primary sintered compact is resintered at a temperature of 800°C. under a dissociated ammonia atmosphere in a mesh belt-type furnace, whereby the sintered layered compact 105A is obtained.
[0080] For example, this sintered layered compact is used as a heat discharging member. In this case, the ceramic layer 101 is contacted to a ceramic product or a ceramic member of which the temperature is increased, and heat dissipating fins are provided to the copper layer 103. When the copper layer is needed having thermal conductivity and electrical conductivity and the ceramic layer 101 is needed having electrical insulation, the copper layer 103 is contacted to a side which must be electrically conductive and the ceramic layer 101 is contacted to a side which must be electrically insulating. Since this sintered layered compact 105A has the copper layer 103 and the ceramic layer 101, the interlayer therebetween is peeled off due to thermal expansion differences therebetween when this sintered layered compact 105A is used in a high temperature atmosphere. Therefore, this sintered layered compact 105A is used at a relatively low temperature at which the above phenomenon does not occur.

[0081] Sintered layered compacts 105B to 105E shown in FIGS. 1B to 1E will be described hereinafter. Production methods for these sintered layered compacts 105B to 105E are the same as that for the sintered layered compact 105A. The following intermediate layer is made of a alumina powder and a copper powder.

[0082] The sintered layered compact 105B is constructed such that two intermediate layers 121 and 123 having different composition from each other are sandwiched between the copper layer 103 and the ceramic layer 101. The intermediate layer 123 on the side of the copper layer 103 is composed of a mixed powder of an alumina powder and a copper powder. The mass ratio of the alumina powder to the copper powder is 15 to 85 in the mixed powder of the intermediate layer 123. That is, the volume ratio of the alumina powder is about 20% in the mixed powder of the intermediate layer 123. The intermediate layer 121 on the side of the ceramic layer 101 is composed of a mixed powder of an alumina powder and a copper powder. The mass ratio of the alumina powder to the copper powder is 30 to 70. That is, the volume ratio of the alumina powder is about 50%. That is, the content of copper is large in the intermediate layer 123 on the side of the copper layer 103, and the content of ceramic is large in the intermediate layer 121 on the side of the ceramic layer 101. This sintered layered compact 105B has a more advantageous structure than the sintered layered compact 105A in relieving thermal stress caused by heat cycling causing surrounding temperature changes and/or repeated thermal stresses.

[0083] The sintered layered compact 105C shown in FIG. 1C is constructed such that the ceramic layer 101 is sandwiched between two copper layers 103a and 103b. The copper layers 103a and 103b are thermally conductive and electrically conductive, and the ceramic layer 101 therebetween is electrically insulating. Therefore, the copper layers 103a and 103b are electrically insulated therebetween by the ceramic layer 101. In this sintered layered compact 105C, for example, heating is performed on the copper layer 103a and heat dissipation is performed on the copper layer 103b so as to have a cooling action. Since the ceramic layer 101 directly contacts the copper layers 103a and 103b, heat resistance characteristics are inadequate, and the sintered layered compact 105C is favorably used at a relatively low temperature or in an environment having low temperature differences.

[0084] The sintered and layered compact 105D as shown in FIG. 5D is constructed such that an intermediate layer 122a is sandwiched between the ceramic layer 101 and the copper layer 103a and an intermediate layer 122b is sandwiched between the ceramic layer 101 and the copper layer 103b in the sintered layered compact 105C. The volume ratio of alumina is about 50% in the intermediate layers 122a and 122b. The sintered and layered compact 105E as shown in FIG. 5E is constructed such that an intermediate layer 121a is sandwiched between the intermediate layer 122a and the ceramic layer 101, an intermediate layer 121b is sandwiched between intermediate layer 122b and the ceramic layer 101, an intermediate layer 123a is sandwiched between intermediate layer 122a and the copper layer 103a, and an intermediate layer 123b is sandwiched between intermediate layer 122b and the copper layer 103b in the sintered layered compact 105D. The volume ratio of alumina is about 70% in the intermediate layers 121a and 121b. The volume ratio of alumina is about 30% in the intermediate layers 123a and 123b. The above, three layers as intermediate layers are disposed between the ceramic layer 101 and the copper layer 103a and between the ceramic layer 101 and the copper layer 103b. In these sintered layered compacts 105D and 105E, intermediate layers are disposed between the ceramic layer 101 and the copper layer 103a and between the ceramic layer 101 and the copper layer 103b, and these sintered layered compacts 105D and 105E have thermal stress relief, thereby giving good heat shock resistance characteristics.

[0085] Next, use examples of the above sintered layered compacts 105A to 105E will be described with reference to FIGS. 2A and 2B. In FIGS. 2A and 2B, reference numeral 105 shows one of the sintered and layered compacts 105A to 105E.

[0086] FIG. 2A shows a cross sectional diagram of a thermoelectric conversion module 106A. The thermoelectric conversion module 106A is constructed such that plural N-type elements and plural P-type elements (thermoelectric elements 108) are positioned so as to alternate with each other, the thermoelectric elements 108 are connected to each other in a line by the sintered layered compacts 105, and the both ends of the sintered layered compacts 105 are sandwiched by metal plates 107 having good thermal conductivity so as to fix the members to each other. For example, the metal plates 107 may be copper plates. The sintered layered compact 105 may be used as a connecting pad. In this thermoelectric conversion module 106A, electricity is generated from a terminal mounted on the end of the thermoelectric element 108 by heating one side thereof and cooling the other side thereof. This thermoelectric conversion module 106A is mounted and used in a state of being disposed between a heat discharging portion of a furnace and a cooling device such as a water jacket.

[0087] In the thermoelectric module 106A as shown in FIG. 2A, the thermoelectric elements 108 and the sintered layered compacts 105 are connected to each other by using solder or graphite coating, so that electrical conductivity and thermal conductivity therebetween are ensured. The sintered layered compacts 105 and the copper plates 107 are connected to each other by using solder or graphite coating, water glass, or high melting point glass, so that thermal conductivity therebetween is ensured. A thermoelectric conversion module 106B shown in FIG. 2B has the same
fundamental structure as that of the thermoelectric conversion module 106A, and bolt 110 and nut 111 for fastening two copper plates 107 hold such that the members thereof are layered and contacted to each other in the thermoelectric conversion module 106B.

[0088] The above sintered layered compacts 105A to 105E can be used as a sintered layered compact 105 used in these thermoelectric conversion modules 106A and 106B. In particular, the sintered layered compacts 105D and 105E are favorably used since the copper layers 103a and 103b have good electrical conductivity and thermal conductivity, the ceramic layer electrically insulates between the copper layers 103a and 103b, thermal stress, which is caused by thermal expansion differences between the high temperature side and the low temperature side and by heat cycling, can be relieved by the intermediate layers 121a, 122a and 123a, and 124a, and generation performance and reliability of these thermoelectric conversion modules 106A and 106B are improved.

[0089] (B) Second Embodiment

[0090] Desirable materials and production method in which the desirable materials are used according to the second embodiment will be described hereinafter. In the second embodiment, description of the same materials and structures as that of the first embodiment are omitted.

[0091] (1) Ceramic Powder

[0092] The same ceramic powder as that of the first embodiment is used.

[0093] (2) Low Melting Powder Added to Ceramic Powder

[0094] A ceramic powder composed of only ceramic powder is hardly sintered when heated to a temperature in which the metal layer is sintered. Due to this, the ceramic layer may possibly collapse when a strong impact is imparted thereto although the ceramic layer may be handled. Therefore, the same low melting point powder as that of the first embodiment is used so as to improve the strength of the ceramic layer.

[0095] (3) Binder for Ceramic Powder

[0096] The same binder for the ceramic powder as that of the first embodiment is used.

[0097] (4) Powder of Metal Layer

[0098] The same powder of the metal layer as that of the first embodiment is used.

[0099] (5) Powder of Intermediate Layer

[0100] The same powder of the intermediate layer as that of the first embodiment is used.

[0101] (6) Lubricant

[0102] The same lubricant as that of the first embodiment is used.

[0103] (7) Multilayered Structure

[0104] The same multilayered structure as that of the first embodiment is used.

[0105] (8) Multilayered Filling of Powder

[0106] The same multilayered filling of the powders as those of the first embodiment are performed.

[0107] (9) Compacting of Powders

[0108] The same compacting of the powders as those of the first embodiment are performed.

[0109] (10) Sintering

[0110] Temperatures of metal-ceramic green compact are about 700 to 950°C when the metal is copper, about 500 to 600°C when the metal is aluminum, about 700 to 850°C when the metal is silver, and about 800 to 1150°C when the metal is nickel. The inside of the heating chamber is in a non-oxidizing gas or in a vacuum when the green compact is sintered. The non-oxidizing gas may be hydrogen, nitrogen, or argon, or a mixed gas of hydrogen and nitrogen. When the metal powder is composed of silver, the green compact can be sintered in air. The lubricant and the binder are dissipated by sintering, and the ceramic layer, the intermediate layer, and the metal layer are sintered. When a low melting point powder such as a soda-lime glass is included in the ceramic layer, the low melting point powder is melted without heating the ceramic layer to a high temperature, and the ceramic layer is sintered and the interface portion between the ceramic layer and the intermediate layer has high bonding strength. In particular, a method in which a low melting point powder is added to the ceramic powder and aluminum having a low melting point is used is favorable since the ceramic layer is sintered at a low temperature without melting the aluminum.

[0111] When sintering is performed, the metal layer is electrically conductive and thermally conductive, and wetability when brazing or adhering by an adhesive agent is performed when using the sintered multilayered compact is ensured.

[0112] Next, the second embodiment of the present invention will be described with reference to the Figures.

[0113] In the second embodiment, a production method of the sintered layered compact 105A shown in FIG. 1A is different from that of the first embodiment. That is, the green compact in the same manner as that of the first embodiment is provided in a sintering furnace, and is sintered at a temperature of 820°C under a dissociated ammonia atmosphere in a mesh belt-type furnace. As a result, the sintered layered compact 105A is constructed in the above manner such that anhydrous borax is melted and alumina is thereby sintered, thereby being integrally sintered and connected. The above second embodiment can be applied to the sintering methods for the sintered layered compacts 105B to 105E shown in FIGS. 1B to 1E.

[0114] (C) Third Embodiment

[0115] Desirable materials and production method in which the desirable materials are used according to the third embodiment will be described hereinafter.

[0116] (1) Metal Powder

[0117] A metal layer having electrical conductivity and thermal conductivity is made of a metal powder. The metal powder is composed of one of copper, aluminum, silver, and nickel, or mixture of at least two of copper, aluminum, silver, and nickel. For example, the mixture is composed of copper and aluminum. These powders have good compressibility, and these powders favorably have predetermined grain sizes so as to pass through a 100-mesh sieve, thereby
being easily filled into a die. When a fine powder is used, flowability can be improved by granulating. These metal powders used in a mixed powder with an electrical insulation powder are selected so that the mixed powder has low segregation degree and good flowability in consideration of grain size distribution of the electrical insulation powder, and commercial and common types used in producing sintered alloy products can be used.

[0118] (2) Electrical Insulating Powder

[0119] A ceramic powder composed of alumina or aluminum nitride which has good electrical insulation characteristics and thermal conductivity characteristics can be used as a simple substance as a powder for forming an electrical insulating layer. Since a sintering of green compacts is performed at temperatures lower than the melting point of included metal therein, a material which is softened or is melted at a sintering temperature and has electrical insulation is favorably mixed into a ceramic powder in the form of a powder, the electrical insulating layer has high strength, and connecting layers thereto is reliably performed. For example, this low melting point powder is boric acid (melting point of 577°C in a state of anhydrous boric acid), anhydrous borax (melting point of 741°C in a state of anhydrous borax), or soda-lime glass (softening point of 500 to 700°C, melting point of about 725°C). When the adding ratio of the low melting point powder is about 0.1 mass % in the ceramic layer, the strength of the ceramic layer is improved. When the adding ratio of the low melting point powder is lower, the liquid phase of the low melting point powder may possibly bubble to the surface of the ceramic layer in sintering the ceramic layer, whereby the adding ratio of the low melting point powder is not more than 50 mass % in the ceramic layer. In the low melting point powder, plural low melting point materials and high melting point materials can be added to a ceramic layer. When the adding ratio of the low melting point powder is about 0.1 mass % in the ceramic layer, the strength of the ceramic layer is improved. When the adding ratio of the low melting point powder is lower, the liquid phase of the low melting point powder may possibly bubble to the surface of the ceramic layer in sintering the ceramic layer, whereby the adding ratio of the low melting point powder is favorably not more than 50 mass % in the ceramic layer.

[0120] The other low melting point material is a glass frit. The glass frit as a glaze for enamel has a vitreous structure composed of SiO₂ as a main component, B₂O₃, MgO, Al₂O₃, and BaO. In the present invention, other commercial kinds of glass frit can be used. The glass frit is melted at temperatures of about 500 to 900°C, and is selected depending on the metal powder used. When the glass frit is added to a ceramic powder at a ratio of 0.1 mass %, the ceramic powder is sintered by melting of the glass frit. As the ratio of the glass frit contains increases, the content of the liquid phase thereof increases in sintering the electrical insulating layer at melting temperatures of the glass frit. In a case in which the content of the liquid phase of the glass frit is extensively generated much, the ceramic powder functions as a frame of the layer, whereby distortion of the layer is inhibited. The electrical insulating layer can be made of only the glass frit in a case in which the sintering temperature is relatively low, the glass frit having a relatively high melting point is used, or the electrical insulating layer is formed thinly.

[0121] Since the glass frit and the mixed powder of the glass frit and the ceramic powder are hard and have low compactibility, a binder such as methyl cellulose (MC), polyvinyl alcohol (PVA), ammonium alginate, carboxymethyl cellulose (CMC), or polyvinyl pyrrolidone (PVP) is mixed into an electrical insulating layer, whereby the green compact can have higher strength. As a result, when the green compact is transferred in processes of powder compacting and of sintering, cracks and defects can be prevented from occurring therein. The above binder dissipates when heated in sintering the electrical insulating layer. Since the density of the electrical insulating layer is reduced and the thermal conductivity thereof is deteriorated when too much of the above binder is added, the mixing ratio of the above binder in the electrical insulating layer is favorably not more than 1 mass %.

[0122] Since the glass frit and the ceramic powder have relatively low flowability, the flowability can be improved by granulating so that powder filling to a die is improved. When the above powders have low flowability due to fine grain size thereof, the above powders are favorably granulated by using a binder such as carboxymethyl cellulose (CMC) so as to have a particle diameter of about 50 to 150 µm, and flowability thereof is thereby improved. As a result, powder filling to a die is easily performed and a green compact has high strength. As compared with a fine ceramic powder, a coarse powder is mixed with the fine powder, sinterability and flowability can thereby be improved.

[0123] (3) Mixed Powder of Metal Powder and Electrical Insulating Powder

[0124] A mixed powder is formed into a functionally gradient layer. For example, the mixed volume ratio of the electrical insulating powder to the metal powder is 1 to 1 in the functionally gradient layer. Alternatively, when the mixed layer is made to have plural layers, a mixed powder including the electrical insulating powder is substantially positioned on the electrical insulating layer, and a mixed powder including the metal powder is substantially positioned away from the electrical insulating layer. For example, when the mixed layer has three layers, the mixed volume ratio of the electrical insulating powder to the metal powder is 75 to 25 in the layer on the side of the electrical insulating layer, is 50 to 50 in the intermediate layer, and is 25 to 75 in the layer on the side of the metal layer.

[0125] (4) Lubricant

[0126] Since the electrical insulating powder is hard, a lubricant such as a metal stearate is favorably added to the electrical insulating powder by not more than about 0.5 mass %, or is coated on an inner wall of a die so that the green compact is easily ejected from the die. The lubricant is coated by electrostatic coating. Alternatively, a lubricant dispersed in liquid is used.

[0127] (5) Filling and Layering of Powders

[0128] A powder feeder can be used for filling each powder in a die having a die for forming an outer portion of a green compact, an upper punch and a lower punch. The powder feeder can be moved forward or backward on a die cavity. Plural powder boxes are connected to the powder feeder in a powder feeding movement direction. For example, when a multilayered structure has a metal layer, a mixed layer, an electrical insulating layer, a mixed layer, and a
metal layer, the powder feeder has three boxes. In this case, a metal powder is filled in the front box, a mixed layer powder is filled in the middle box, and an electrical insulating powder is filled in the rear box. The powder feeder is moved forward in a state in which the lower punch is flush with the upper face of the die, so that the powder box having the metal powder is stopped on the lower punch, and then the lower punch or the die is moved so as to form a cavity, whereby the metal powder is filled therein. Next, the box having the mixed layer powder is moved on the die cavity, and then the mixed powder is filled in the same manner as that of the metal powder. After the electrical insulating powder is filled in the same manner as that of the metal powder, the powder feeder is moved in turn backward, and multilayered filling of five layers can be performed.

[0129] A powder feeder has a structure such that spaces are provided between plural powder boxes. In this case, after one kind of powder is filled in the cavity, in a state in which the space is stopped on the cavity, the filled powder is dropped, the cavity is formed, and the filled powder adhered on the wall surface of the die cavity is scratched and dropped by using a simple punch. As a result, a green compact having a multilayered structure which is distinctively divided can be obtained.

[0130] Since surfaces of the filled powders have microscopic rough portions, the powders adjacent to each other have slightly mixed portion with each other. As a result, the compositions of the layers are not distinctively divided from each other, and the layers adjacent to each other are mixed so as to be connected to each other, and each layer is difficult to peel off from the green compact.

[0131] (6) Compacting of Powders

[0132] Compacting is performed on the metal powders of the above metal powders as described below. That is, compacting is performed on the copper powder, the silver powder, and the aluminum powder at a compacting pressure of about 100 to 300 MPa, and is performed on the nickel powder at a compacting pressure of about 400 MPa of the above metal powders, whereby the green compacts of these metal powders have a relative density of not less than 95% and thereby have good electrical conductivity and good thermal conductivity. On the other hand, when compacting is performed on the electrical insulating powder of alumina at a compacting pressure of about 600 MPa, the green compact of the electrical insulating powder of alumina has a relative density of about 50%. When compacting is performed on the electrical insulating powder at a compacting pressure of 700 MPa, the green compact of the electrical insulating powder has a relative density of about 60%. The compacting pressure of the multilayered powders is favorably about 700 to 1000 MPa since the relative density of the green compact of the electrical insulating powder gradually increases when compacting is performed on the electrical insulating powder at a compacting pressure of more than 700 MPa.

[0133] (7) Multilayered Structure

[0134] A multilayered structure of a thermal stress relief pad has an electrical insulating layer which is at a middle portion in a thickness direction and mixed layers which are formed on the both sides of the electrical insulating layer. The electrical insulating layer has a thickness of 0.5 to 2 mm so that thermal conductivity and electrical insulation of the electrical insulating layer are ensured. The mixed layer is layered such that the content of the electrical insulating powder is large on the side of the electrical insulating layer and the content of the metal powder is large on the side away from the electrical insulating layer. Alternatively, a thermal stress relief pad has a multilayered structure such that the metal layer is provided on at least one of the outsides of the mixed layer. One metal layer is used as an electrode which connects thermoelectric conversion elements. When electrodes are separately produced and thermoelectric conversion elements are assembled, the multilayered structure may have no metal layer.

[0135] (6) Sintering

[0136] The same continuous sintering furnace as that used in producing sintered metal products is used in sintering. Alternatively, microwave sintering or plasma sintering can be performed. A typical mesh belt-type continuous furnace is favorable since sintering can be performed efficiently. Sintering is performed in a non-oxidizing gas or in a vacuum when the green compacts are sintered. The non-oxidizing gas is hydrogen, or nitrogen, argon, or a mixed gas of hydrogen and nitrogen. When the metal powder is composed of silver, the green compact can be sintered in air. The temperatures of sintering is about 700 to 950°C when the metal is copper, is about 500 to 600°C when the metal is aluminum, is about 700 to 950°C when the metal is silver, and is about 800 to 1150°C when the metal is nickel. The kind of enamel frit for sintering or for melting is selected in accordance with the above temperature range.

[0137] The lubricant and the binder are dissipated by sintering, the metal layer, the mixed layer, and the electrical insulating layer are sintered, and each interlayer therebetween is strongly connected to each other. The glass frit of the electrical insulating layer is sintered or melted, is enameled and is adhered closely to the mixed layer. When the electrical insulating powder of the mixed layer is only the ceramic powder, the ceramic dispersed sintered metal composite material is formed. When only glass frit is included in the electrical insulating powder in the mixed layer, the glass frit is softened or melted, whereby sintering the mixed layer can be performed more quickly.

[0138] Next, the third embodiment of the present invention will be described hereinafter with reference to Figures. FIG. 3 is a cross sectional diagram showing a thermal stress relief pad 301A for thermoelectric conversion elements. The thermal stress relief pad 301A has an electrical insulating layer 302 and mixed layers 303 having plural mixed layers layered on the both sides of the electrical insulating layer 302, metal layers 304 which are made of only copper and are layered as an outermost layer thereof. The mixed layer 303 has a structure such that a first mixed layer 331, a second mixed layer 332, and a third mixed layer 333 are layered in turn on the side of the electrical insulating layer 302. The content volume ratio of copper is small in the first mixed layer 331, the content ratio of copper to electrical insulating material is 1:1 in the second mixed layer 332, and the content of copper is large in the third mixed layer 333.

[0139] The following powders are used for producing this thermal stress relief pad 301A.

[0140] (a) copper powder (for forming the metal layer 304)
[0141] (b) mixed powder (for forming the first mixed layer 331) of a copper powder and an alumina powder (ratio of the copper powder to the alumina powder is 50:50, that is, the volume ratio of alumina is about 70%)

[0142] (c) mixed powder (for forming the second mixed layer 332) of a copper powder and an alumina powder (ratio of the copper powder to the alumina powder is 30:70, that is, volume ratio of alumina is about 50%)

[0143] (d) mixed powder (for forming the second mixed layer 333) of a copper powder and an alumina powder (ratio of the copper powder to the alumina powder is 15:85, that is, volume ratio of alumina is about 30%)

[0144] (e) ceramic powder (for forming the electrical insulating layer 302) composed of an electrical insulating powder of an alumina powder and an enamel frit; the electrical insulating powder including methyl cellulose at ratio of 0.1 mass % (weight ratio of the alumina powder to the enamel frit powder is 1:1)

[0145] A vitreous powder composed of SiO₂, and/or B₂O₃ as a main component is used as an enamel frit. SiO₂ and/or B₂O₃ start melting at a temperature of 700°C, and show a melted state in which they are wet and spread on the copper plate when heated on the copper plate under a dissociated ammonia gas.

[0146] Next, the above powders are filled in turn into a cavity for a die in a layering direction, and then compacting is performed on the multilayered powders at a compacting pressure of 700 to 1000 MPa, whereby a green compact is obtained. In this case, when the above powders are filled into the die, a zinc stearate powder is coated by electrostatic coating on an inner wall of the cavity, and then the above powders are filled thereto in turn by using a feeder. After compacting is simultaneously performed on all the multilayered powders in the above manner, the green compact is ejected from the die, and is then sintered. For example, the sintering is performed on the green compact by heating at a temperature of 800°C under a dissociated ammonia gas.

[0147] When the above processes of multilayered filling, compacting, and sintering are performed, a sintered compact shown in FIG. 4 is often obtained. That is, a thin copper foil portion 305 is formed in this sintered compact on a surface of a side of the electrical insulating layer 302 (on a side of the inner wall face of the die). The mixed layers 303 are electrically short-circuited by the copper foil portion 305, and the electrical insulating layer 302 does not perform an electrical insulating function. The reason that the copper foil portion 305 is formed is thought to be that, when multilayered filling is performed on the above powders in the die in turn, the metal of the metal powder containing layer, which is filled before the electrical insulating powder is filled therein, is adhered to the inner wall face of the die, and then the electrical insulating layer is moved thereto, whereby the side of the electrical insulating layer 302 is covered with the metal powder.

[0148] Therefore, the following stepwise production method is used for maintaining the electrical insulating function of the electrical insulating layer 302.

[0149] FIGS. 5A and 5B show raw materials 310a and 310b of the green compact, which are referred to simply as “compressed materials 310a and 310b”. The electrical insulating powder, the various mixed powders, and the copper powder are layered, and are compacted, whereby the compressed material 310a is obtained. The compressed material 310a is a green compact having the electrical insulating layer 302 and the mixed layer 303 which has the first mixed layer 331, the second mixed layer 332 and the third mixed layer 333 in turn from the bottom, and the metal layer 304. Since compacting is performed in a state in which the electrical insulating layer 302 is positioned at bottom, the side of the electrical insulating layer 302 is not contaminated by the mixed powders and/or the metal powders and is not adhered thereby when the above compacting is performed, whereby forming the copper foil portion 305 shown in FIG. 4 is prevented and the side of the electrical insulating layer 302 is exposed. Next, the mixed layer 303 of the compressed material 310b is contacted to the side of the electrical insulating layer 302 of the compressed material 310a, and then sintering is performed thereon while maintaining the state of contact thereof. As a result, contacting interfaces of the mixed layer 303 of the compressed material 310b and the electrical insulating layer 302 of the compressed material 310a are connected to each other, and the thermal stress relief pad 301A shown in FIG. 6A is produced. According to this thermal stress relief pad 301A, the electrical insulating function of the electrical insulating layer 302 is ensured and electrical short-circuiting does not occur since forming the copper foil portion 305 shown in FIG. 4 is prevented on the side of the electrical insulating layer 302 of the compressed material 310a.

[0150] The other method for securing the electrical insulating characteristics of the electrical insulating layer 302 is as follows. That is, as shown in FIG. 4, a surface portion P-P which is thicker than the copper foil portion 305 on a side of the sintered compact is removed by cutting or by polishing. As a result, the copper foil portion 305 causing a short-circuit is removed, and the electrical insulating layer 302 is exposed on the side of the thermal stress relief pad 301A.

[0151] The thermal stress relief pad 301A shown in FIGS. 3 and 5A is one example of the present invention, and FIGS. 6B to 6G show thermal stress relief pads 301B to 301G. FIGS. 5C and 5D show other compressed materials 310c and 310d.

[0152] The electrical insulating powder and the various mixed powders are filled, are layered, and are compacted, whereby the compressed material 310c is obtained. The compressed material 310c shown in FIG. 5C is a green compact having the electrical insulating layer 302 and the mixed layer 303 which has the first mixed layer 331, the second mixed layer 332, and the third mixed layer 333 in turn from the bottom. The electrical insulating powder and the various mixed powders are filled, are layered, and are compacted, whereby the compressed material 310d is obtained. The compressed material 310d shown in FIG. 5D is a green compact having only the mixed layer 303 which has the first mixed layer 331, the second mixed layer 332 and the third mixed layer 333 in turn from the bottom.

[0153] Two kinds of compressed materials are appropriately selected from the compressed materials 310a to 310d.
shown in FIGS. 5A to 5D, and sintering is performed on the selected kinds of compressed materials, whereby the thermal stress relief pads 301B to 301G shown in FIGS. 6B to 6G can be produced. The thermal stress relief pad 301B shown in FIG. 6B is produced such that two compressed materials 310c are stacked so that the electrical insulating layers 302 thereof contact each other and are sintered. The thermal stress relief pad 301C shown in FIG. 6C is produced such that compressed materials 310a and 310c are stacked so that the electrical insulating layers 302 thereof contact each other and are sintered. The thermal stress relief pad 301D shown in FIG. 6D is produced such that the electrical insulating layer 302 of the compressed material 310c and the compressed material 310d are stacked on each other and are sintered. The thermal stress relief pad 301E shown in FIG. 6E is produced such that the electrical insulating layer 302 of the compressed material 310c and the mixed layer 303 of the compressed material 310b are stacked and are sintered. The thermal stress relief pad 301F shown in FIG. 6F is produced such that the electrical insulating layers 302 of the compressed materials 310a are stacked and are sintered. The thermal stress relief pad 301F shown in FIG. 6F is produced such that the electrical insulating layer 302 of the compressed material 310a and the compressed material 310d are stacked and are sintered.

[0154] In the thermal stress relief pads 301B to 301G, two of the compressed materials 310a to 310d which are compacted beforehand are appropriately selected and sintered in the same manner as the case of the thermal stress relief pad 301A, whereby formation of the copper foil portion 305 which may cause a short-circuit is prevented, and the electrical insulating function of the electrical insulating layer 302 is secured.

[0155] A use example of the above thermal stress relief pad 301A will be described hereinafter with reference to FIG. 7. The thermal stress relief pads 301B to 301G can be used appropriately instead of the thermal stress relief pad 301A.

[0156] FIG. 7 shows a cross sectional diagram of a thermoelectric conversion module 307. The thermoelectric conversion module 307 is constructed such that plural N-type elements and plural P-type elements (thermoelectric elements 305) are positioned so as to alternate with each other, the thermoelectric elements 305 are connected to each other in series by the metal layers 304 of the thermal stress relief pads 301A, and the both ends of the thermal stress relief pads 301A are sandwiched by metal plates 306 having good thermal conductivity so as to fix the members to each other. For example, the metal plates 306 are copper plates.

[0157] The thermal stress relief pads 301A are connected to the thermoelectric conversion elements 305 by using solder or a graphite coating so that electrical conductivity and thermal conductivity therebetween are ensured, and are connected to the copper plates 306 by using solder or a graphite coating, water glass, or high melting point glass, so that thermal conductivity therebetween is ensured. Alternatively, instead of using the above adhesive agents, a bolt and a nut for fastening two copper plates 306 hold such that the members thereof are layered and contacted to each other in the thermoelectric conversion module 307. In this thermoelectric conversion module 307, electricity is generated from a terminal mounted on the end of the thermoelectric element 305 by heating one side thereof and cooling the other side thereof. This thermoelectric conversion module 307 is mounted and used in a state of being disposed between a heat discharging portion of a furnace and a cooling device such as a water jacket.

[0158] When the thermoelectric conversion module 307 is used, the metal layer 304 contacting the thermoelectric conversion element 305 of the thermal stress relief pad 301A is an electrode member and a heat conducting member. The electrical insulating layer 302 prevents electrical leakage to the sides of the copper plates 306. The thermal expansion coefficient of the mixed layer 303 is different from that of the metal layer 304 or the copper plates 306. As a result, thermal stress, which is caused by thermal expansion difference between the high temperature side and the low temperature side and by heat cycling, can be relieved and generation performance and reliability of the thermoelectric conversion module 307 is improved.

[0159] (D) Fourth Embodiment

[0160] Desirable materials and production method in which the desirable materials are used according to the fourth embodiment will be described hereinafter. In the fourth embodiment, description of the same materials and structures as that of the third embodiment are omitted.

[0161] (1) Metal Powder

[0162] The same metal powder as that of the third embodiment is used. The same powder, which is mixed into an electrical insulating material powder as that of the third embodiment, is used. The electrical insulating material powder is composed of the following ceramics powder and the following glass frit, and is used instead of the electrical insulating powder, which is composed of the ceramics and the low melting point material such as boric acid or is composed of the ceramics and the glass frit, of the third embodiment.

[0163] (2) Ceramic Powder

[0164] A ceramic powder is composed of alumina or aluminum nitride, which has good electrical insulation and good thermal conductivity. In this case, in particular, alumina has better powder compression compactibility than that of aluminum nitride, and has a lower melting point than that of aluminum nitride, whereby being favorably used. The ceramic powder is used as a mixed powder with a metal powder or as described below glass frit. When the ceramic powder is added to the mixed powder, the ceramic powder favorably has a grain size approximate to that of the metal powder so that the ceramic powder is equally dispersed in the metal powder and the metal powder is sintered.

[0165] (3) Glass Frit

[0166] The glass frit has a vitreous structure composed of SiO₂, B₂O₃, P₂O₅, Al₂O₃, ZnO as a main component, and includes MgO, TiO₂, Bi₂O₃, or CaO if necessary. The glass frit does not have electrical conductivity. For example, the glass frit may be an oxide glass which is widely used as a glass in practice, special glass such as an oxidized glass in which a part of oxygen is substituted by nitrogen, glaze used for enamel, cloisonné and ceramic, solder glass used for sealing or adhering, or binder for a baking finish. Various kinds of the above glass frits are sold commercially. For example, a glass frit for a porcelain covering is disclosed in

[0167] The glass frits have softening points of not less than about 350°C. In consideration of viscosity of the glass frit when softened and melted, wettablility of the glass frit with metal and thickness of the electrical insulating layer, the kind of the glass frit is selected from glass frits having softening points of about 500 to 900°C, and whether or not only glass frit is used and whether a ceramic is mixed into the glass frit are determined depending on sintering temperature of the metal for thermal stress relief pads. Borate glass or glaze for enamel is favorably used from a standpoint of adhesiveness thereof with metal.

[0168] (4) Powder for Forming Electrical Layer

[0169] A glass frit as a simple substance or a mixture of a ceramic powder and a glass frit is used as a powder for forming the electrical insulating layer. When the glass frit as a simple substance is used, the electrical insulating layer is sintered at a temperature at which the glass frit is melted and flowed freely, whereby the glass frit is flowed out of the outer portion of the multilayered compact so that the electrical insulating layer is made much thinner. In this case, since there may be a case in which the electrical insulating layer breaks, the sintering temperature thereof is not more than the softening point thereof. When the electrical insulating layer is sintered at a temperature in which the glass frit is melted, the glass frit is favorably mixed with a ceramic powder such as an alumina powder or aluminum nitride. As a result, the ceramic powder functions as a frame of the electrical insulating layer so as to maintain the melted glass frit, the electrical insulating layer is sintered, and the electrical insulating layer and the layers adjacent thereto are connected reliably. When the glass frit is added to the ceramic powder at a ratio of 0.1 mass %, the green compact of the ceramic powder is sintered in a state in which the glass frit is in a liquid phase. When the included ratio of the glass frit is larger, the liquid phase of the glass frit increases by sintering, the electrical insulating layer is sintered well and is strongly adhered to the composite layers adjacent thereto.

[0170] (5) Binder for Forming Electrical Insulating Layer and Granulating Thereof

[0171] Since the glass frit and the mixed powder of the glass frit and the ceramic powder are hard and are relatively fine, these materials have low strength in the green compact, and care in handling is needed. Therefore, the same binder as that of the third embodiment is used, and the same method of granulation as that of the third embodiment is used so that the green compact has high strength.

[0172] (6) Mixed Powder of Metal Powder and Electrical Insulating Powder

[0173] A mixed powder is formed as an graded function layer. The mixed powder is a mixed powder of the metal powder and the ceramic powder, a mixed powder of the metal powder and the glass frit, or a mixed powder of the metal powder, the ceramic powder and the glass frit. For example, the mixed volume ratio of the metal powder to the electrical insulating powder is 1 to 1 in the mixed layer. Alternatively, when the mixed layer is made to have plural layers, a mixed powder including the electrical insulating material powder is substantially positioned on the electrical insulating layer, and a mixed powder including the metal powder is substantially positioned away from the electrical insulating layer. For example, when the mixed layer has three layers, the mixed volume ratio of the electrical insulating material powder to the metal powder is 75 to 25 in the layer on the side of the electrical insulating layer, is 50 to 50 in the intermediate layer, and is 25 to 75 in the layer on the side of the metal layer.

[0174] (7) Lubricant

[0175] Since the electrical insulating material powder is hard, a lubricant such as a metal stearate is favorably coated on an inner wall of a die so that the green compact is easily ejected from the die. The lubricant is coated by electrostatic coating. Alternatively, the lubricant dispersed in a liquid is used.

[0176] (8) Filling and Layering of Powders

[0177] The same filling and layering of powders as those of the third embodiment are used other than using the electrical insulating material powder instead of the electrical insulating powder of the third embodiment.

[0178] (9) Compacting of Powders

[0179] The same compacting of powders as those of the third embodiment are used.

[0180] (10) Multilayered Structure

[0181] The multilayered structure is shown in (a) to (f). The mixed powder of the metal powder and the electrical insulating material powder includes a powder having one kind of component or more kinds thereof.

[0182] (a) mixed layer

[0183] (b) metal layer-mixed layer

[0184] (c) mixed layer-electrical insulating layer

[0185] (d) metal layer-mixed layer-electrical insulating layer

[0186] (e) mixed layer-electrical insulating layer-mixed layer

[0187] (f) metal layer-mixed layer-electrical insulating layer-mixed layer-metal layer

[0188] A thermal stress relief pad is produced by appropriately using the structures shown in (a) to (f). For example, a thermal stress relief pad is produced such that an electrical insulating material powder is coated on surfaces of mixed layers of two green compacts and the green compacts are sintered and connected in a state in which the electrical insulating layer is disposed therebetween. In this case, the structure shown in (a) or (b) is used as the green compact. For example, a thermal stress relief pad is produced such that two green compacts, which have half thickness including the electrical insulating material powder, are sintered and connected in a state in which the electrical insulating layer is disposed therebetween. In this case, the structure shown in (c) or (d) is used as the green compact. The
structures shown in (a) or (b) can be used as one of the above green compacts. A thermal stress relief pad can be produced by sintering in a state of green compact having the structure shown in (e) or (f).

[0190] Coating an electrical insulating material powder to the green compact of only the mixed powder shown in the above (a) or on the green compact of the metal layer and the mixed layer shown in the above (b) can be performed in a state of a powder or slurry thereof. A method in which the electrical insulating material powder is dropped from a sieve to the side of the mixed layer of the green compact which is mounted at top and then the other green compact is mounted thereon so that the electrical insulating material powder is disposed therebetweent is used. Alternatively, a method in which pasted liquid of the above CMC or the above PVA is coated on the mixed layer of the green compact and then the other green compact is mounted thereon so that the electrical insulating material powder is disposed therebetweent is used. The slurry of the electrical insulating material powder is commercial enamel liquid (glaze slurry), organic solvent such as mineral oil, liquid paraffin, alcohol, or acetone, or mixed dispersed liquid of PVA or CMC.

[0191] (12) Sintering

[0192] The same sintering as that of the third embodiment is used.

[0193] Next, the fourth embodiment of the present invention will be described with reference to the Figures.

[0194] FIGS. 8A to 8C are cross sectional diagrams showing thermal stress relief pads 401A to 401C for thermoelectric conversion elements. In the thermal stress relief pads 401A to 401C, the metal is copper, and the ceramic is alumina and/or enamel frit.

[0195] The thermal stress relief pad 401A shown in FIG. 8A has an electrical insulating layer 402 at a center portion in a thickness direction, and mixed layers 403 having plural mixed layers on both sides of the electrical insulating layer 402. The mixed layer 403 has a structure such that a first mixed layer 431, a second mixed layer 432, and a third mixed layer 433 are layered in turn on the side of the electrical insulating layer 402. The content ratio of copper is small in the first mixed layer 431, the volume content ratio of copper to electrical insulating material is 1:1 in the second mixed layer 432, and the content of copper is large in the third mixed layer 433. The thermal stress relief pad 401B shown in FIG. 8B has a structure such that metal layers 404 made only of copper are layered on both surfaces of thermal stress relief pad 401A shown in FIG. 8A. The thermal stress relief pad 401C shown in FIG. 8C has a structure such that a metal layer 404 made only of copper is layered on one of the surfaces of the thermal stress relief pad 401A shown in FIG. 8A. In FIG. 8C, the metal layer 404 made only of copper is layered on the bottom surface of the thermal stress relief pad 401A shown in FIG. 8A.

[0196] The powders used for producing the above thermal stress relief pads 401A to 401C are the same as those of the third embodiment.

[0197] For example, three method, as shown in FIGS. 9A to 9C, are used as a compacting of powders. In all cases, a zinc stearate powder is coated by electrostatic coating on an inner wall of the cavity, the above powders are filled thereto in turn by using a feeder, and then are compacted at a pressure of 700 MPa. These methods can be used for compacting the thermal stress relief pads 401A and 401C shown in FIGS. 8A and 8C instead of the thermal stress relief pad 401B shown in FIG. 8B.

[0198] FIG. 9A shows a method in which, when compacting is performed on powders, all used powders are filled and layered so that the powders are simultaneously and integrally compacted, and then are sintered. FIG. 9B shows a method in which, when compacting is performed on powders, two green compacts having the electrical insulating layer 402, the mixed layer 403 and the metal layer 404 are obtained and then sintered in a state in which the electrical insulating layers 402 are contacted to each other. In this case, one of the green compacts may not have the electrical insulating layer 402. FIG. 9C shows a method in which, after two green compacts having the mixed layer 403 and the metal layer 404 are obtained, the electrical insulating layer 402 is formed by coating the electrical insulating material powder on the surface of the mixed layer 403 of one green compact, the other green compact is mounted on the electrical insulating layer 402 of one green compact, and then they sintered.

[0199] The above thermal stress relief pads 401A to 401C can be applied to the thermoelectric conversion module 302 in the same manner as thermal stress relief pads 301A to 301F of the third embodiment.

[0200] When the thermal stress relief pads 401A and 401C are used, the thermoelectric conversion elements 305 are connected by a conductive member corresponding to the metal layer 404, and the surface of the mixed layer 403 is contacted to the conductive member.

What is claimed is:

1. A production method for a sintered metal-ceramic layered compact, comprising steps of:
   filling and layering a metal powder and a ceramic powder, or
   filling and layering a metal powder, a mixed powder of a metal powder and a ceramic powder, and a ceramic powder;
   forming a green compact of the layered powders by compacting the layered powders; and
   sintering a layer including the metal of the green compact at a temperature of lower than a melting point of the metal by heating by irradiation of microwaves in a non-oxidizing atmosphere.

2. The production method for a sintered metal-ceramic layered compact according to claim 1,
   wherein the production method uses a microwave heating furnace provided with a cooling device, and
   a side of the metal layer of the compact is contacted to the cooling device of the microwave heating furnace in the step of sintering the green compact.

3. The production method for a sintered metal-ceramic layered compact according to claim 1,
wherein the metal is selected from a group consisting of copper, aluminum, silver, and nickel, or a mixture thereof, and

the ceramic is alumina or aluminum nitride.

4. The production method for a sintered metal-ceramic layered compact according to claim 1,

wherein the ceramic powder includes at least one low melting point powder selected from a group consisting of boric acid, anhydrous borax, sodium triboric acid, sodium pentaboric acid, and soda-lime glass, and

the low melting point powder is mixed in a ratio of not more than 50 mass % in the ceramic powder.

5. The production method for a sintered metal-ceramic layered compact according to claim 1,

wherein the ceramic powder includes at least one binder selected from a group consisting of methyl cellulose (MC), polyvinyl alcohol (PVA), ammonium alginate acid, carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), and polyvinyl pyrrolidone (PVP), and

the binder is mixed in a ratio of not more than 1 mass % in the ceramic powder.

6. The production method for a sintered metal-ceramic layered compact according to claim 5,

wherein the mixed powder of the ceramic powder and the binder is granulated to have a particle diameter of not more than 150 μm.

7. The production method for a sintered metal-ceramic layered compact according to claim 1,

wherein the mixed powder of the metal powder and the ceramic powder has two or more mixed powders which have different compositions from each other, wherein

the metal is mixed in a volume not less than that of the ceramic powder in the mixed powder disposed on the side of the metal layer, and

the ceramic powder is mixed in a volume not less than that of the metal powder in the mixed powder disposed on the side of the ceramic layer.

8. A production method for a sintered metal-ceramic layered compact, comprising steps of:

filling and layering a metal powder and a ceramic powder, or

filling and layering a metal powder, a mixed powder of a metal powder and a ceramic powder, and a ceramic powder;

forming a green compact of the layered powders by compacting the layered powders;

presintering a layer including the metal of the compact at a temperature lower than a melting point of the metal by heating by irradiation of microwaves in a non-oxidizing atmosphere; and

resintering the presintered compact at a temperature lower than a melting point of the metal in a non-oxidizing atmosphere.

9. The production method for a sintered metal-ceramic layered compact according to claim 8,

wherein the production method uses a microwave heating furnace provided with a cooling device, and

a side of the metal layer of the compact is contacted to the cooling device of the microwave heating furnace in the step of sintering the compact.

10. The production method for a sintered metal-ceramic layered compact according to claim 8,

wherein the metal is selected from a group consisting of copper, aluminum, silver, and nickel, or a mixture thereof, and

the ceramic is alumina or aluminum nitride.

11. The production method for a sintered metal-ceramic layered compact according to claim 8,

wherein the ceramic powder includes at least one low melting point powder selected from a group consisting of boric acid, anhydrous borax, sodium triboric acid, sodium pentaboric acid, and soda-lime glass, and

the low melting point powder is mixed in a ratio of not more than 50 mass % in the ceramic powder.

12. The production method for a sintered metal-ceramic layered compact according to claim 8,

wherein the ceramic powder includes at least one binder selected from a group consisting of methyl cellulose (MC), polyvinyl alcohol (PVA), ammonium alginate acid, carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), and polyvinyl pyrrolidone (PVP), and

the binder is mixed in a ratio of not more than 1 mass % in the ceramic powder.

13. The production method for a sintered metal-ceramic layered compact according to claim 12,

wherein the mixed powder of the ceramic powder and the binder is granulated to have a particle diameter of not more than 150 μm.

14. The production method for a sintered metal-ceramic layered compact according to claim 8,

wherein the mixed powder of the metal powder and the ceramic powder has two or more mixed powders which have different compositions from each other, wherein

the metal is mixed in a volume not less than that of the ceramic powder in the mixed powder disposed on the side of the metal layer, and

the ceramic powder is mixed in a volume not less than that of the metal powder in the mixed powder disposed on the side of the ceramic layer.

15. A production method for a sintered metal-ceramic layered compact, comprising steps of:

filling and layering a metal powder and a ceramic powder, or

filling and layering a metal powder, a mixed powder of a metal powder and a ceramic powder, and a ceramic powder;

forming a green compact of the layered powders by compacting the layered powders;

presintering a layer including the metal of the compact at a temperature lower than a melting point of the metal by heating by irradiation of microwaves in a non-oxidizing atmosphere; and

resintering the presintered compact at a temperature lower than a melting point of the metal in a non-oxidizing atmosphere.

16. The production method for a sintered metal-ceramic layered compact according to claim 15,
wherein the metal is selected from a group consisting of copper, aluminum, silver, and nickel, or a mixture thereof, and

the ceramic is alumina or aluminum nitride.

17. The production method for a sintered metal-ceramic layered compact according to claim 15,

wherein the ceramic powder includes at least one low melting point powder selected from a group consisting of boric acid, anhydrous borax, sodium triboric acid, sodium pentaboric acid, and soda-lime glass, and

the low melting point powder is mixed in a ratio of not more than 50 mass % in the ceramic powder.

18. The production method for a sintered metal-ceramic layered compact according to claim 15,

wherein the ceramic powder includes at least one binder selected from a group consisting of methyl cellulose (MC), polyvinyl alcohol (PVA), ammonium alginate acid, carboxymethyl cellulose (CMC), hydroxyethyl cellulose (EC), and polyvinyl pyrrolidone (PVP), and

the binder is mixed in a ratio of not more than 1 mass % in the ceramic powder.

19. The production method for a sintered metal-ceramic layered compact according to claim 18,

wherein the mixed powder of the ceramic powder and the binder is granulated to have a particle diameter of not more than 150 μm.

20. The production method for a sintered metal-ceramic layered compact according to claim 15,

wherein the mixed powder of the metal powder and the ceramic powder has two or more mixed powders which have different compositions from each other, wherein

the metal is mixed in a volume not less than that of the ceramic powder in the mixed powder disposed on the side of the metal layer, and

the ceramic powder is mixed in a volume not less than that of the metal powder in the mixed powder disposed on the side of the ceramic layer.

21. A production method for a thermal stress relief pad for thermoelectric conversion elements, comprising steps of:

filling and layering an electrical insulating powder (30C) and a mixed powder (30B) of a metal powder and an electrical insulating powder in turn in a cavity of a die, and forming a green compact (31) of the layered powders by compacting the layered powders, or

filling and layering an electrical insulating powder (30C), a mixed powder (30B) of a metal powder and an electrical insulating powder, and a metal powder (30A) in turn in a cavity of a die, and forming a green compact (32) of the layered powders by compacting the layered powders; and

contacting an electrical insulating layer, which is made of the electrical insulating powder (30C) in either the green compact (31) or the green compact (32), to a surface of an electrical insulating layer of the electrical insulating powder (30C) in either the green compact (31) or the green compact (32); or

filling a mixed powder (30B) of a metal powder and a ceramic powder in a cavity of a die, and forming a green compact (33) by compacting the powder, and contacting an electrical insulating layer, which is made of the electrical insulating powder (30C) in either the green compact (31) or the green compact (32), to a surface of the green compact (33), or

filling and layering a metal powder (30A) and a mixed powder (30B) of a metal powder and an electrical insulating powder in turn in a cavity of a die, and forming a green compact (34) of the layered powders by compacting the layered powders, and contacting an electrical insulating layer, which is made of the electrical insulating powder (30C) in either the green compact (31) or the green compact (32), to a surface of the green compact (34), and

sintering the green compacts, which are in the above contacting state to each other, at a temperature lower than a melting point of the included metal in a non-oxidizing atmosphere.

22. The production method for a thermal stress relief pad for thermoelectric conversion elements, according to claim 21,

wherein the electrical insulating powder is a mixed powder (30C1), a mixed powder (30C2), or a glass frit powder (30C3),

wherein the mixed powder (30C1) is composed of one of an alumina powder and an aluminum nitride powder, and one low melting point electrical insulating powder selected from a group consisting of boric acid, sodium borate, and soda-lime glass, the low melting point electrical insulating powder being mixed in a ratio of not more than 50 mass %,

the mixed powder (30C2) is composed of one of an alumina powder and an aluminum nitride powder and a glass frit which is mixed in a ratio of not less than 0.1 mass %, and

the metal powder (30A) is selected from a group consisting copper, aluminum, silver, and nickel, or a mixture thereof.

23. A production method for a thermal stress relief pad for thermoelectric conversion elements, comprising steps of:

filling and layering a mixed powder (30B) of a metal powder and an electrical insulating powder, an electrical insulating powder (30C), and a mixed powder (30B) of a metal powder and an electrical insulating powder in turn in a cavity of a die, or

filling and layering a metal powder (30A), a mixed powder (30B) of a metal powder and an electrical insulating powder, an electrical insulating powder (30C), a mixed powder (30B) of a metal powder and an electrical insulating powder, and a metal powder (30A) in turn in a cavity of a die;

forming a green compact of the layered powders by compacting the layered powders,

sintering the green compact at a temperature lower than a melting point of the included metal powder in a non-oxidizing atmosphere; and

removing a side surface portion of the sintered compact by cutting or by polishing.
24. The production method for a thermal stress relief pad for thermoelectric conversion elements, according to claim 23,

wherein the electrical insulating powder is a mixed powder (30C1), a mixed powder (30C2), or a glass frit powder (30C3),

wherein the mixed powder (30C1) is composed of one of an alumina powder and an aluminum nitride powder, and one low melting point electrical insulating powder selected from a group consisting of boric acid, sodium boric acid, and soda-lime glass, one low melting point electrical insulating powder being mixed in a ratio of not more than 50 mass %,

the mixed powder (30C2) is composed of one of an alumina powder and an aluminum nitride powder and a glass frit which is mixed in a ratio of not less than 0.1 mass %, and

the metal powder (30A) is selected from a group consisting copper, aluminum, silver, and nickel, or a mixture thereof.

25. A production method for a thermal stress relief pad for thermoelectric conversion elements, comprising steps of:

filling and layering an electrical insulating material powder (40A) for an electrical insulating layer and a mixed powder (40B) of a metal powder and an electrical insulating material powder in a die, or

filling and layering an electrical insulating material powder (40A) for an electrical insulating layer, a mixed powder (40B) of a metal powder and an electrical insulating material powder, and a metal powder (40C) in a die;

forming a green compact of the layered powders by compacting the layered powders; and

sintering the green compact at a temperature lower than a melting point of the included metal powder in a non-oxidizing atmosphere,

wherein the metal powder is selected from a group consisting of copper, aluminum, silver and nickel, or a mixture thereof,

the electrical insulating material powder (40A) is selected from a group consisting of a glass frit (40A1) and a mixed powder (40A2) of a ceramic powder and a glass frit, the ceramic powder being composed of alumina or aluminum nitride,

the electrical insulating material powder (40A) included in the mixed powder (40B) is selected from a group consisting of a ceramic powder, the glass frit (40A1), and a mixed powder (40A2) of a ceramic powder and a glass frit, the ceramic powder being composed of alumina or aluminum nitride.

26. The production method for a thermal stress relief pad for thermoelectric conversion elements according to claim 25,

wherein the electrical insulating material powder (40A) is a mixed powder (40A2) of the ceramic powder and the glass frit, and

the glass frit is mixed in a ratio of not less than 0.1 mass % in the mixed powder (40A2).

27. The production method for a thermal stress relief pad for thermoelectric conversion elements according to claim 25,

wherein the mixed powder (40B), the electrical insulating material powder (40A) and the mixed powder (40B) are layered in turn in the die in the step of filling and layering powders, or

the metal powder (40C), the mixed powder (40B), the electrical insulating material powder (40A), the mixed powder (40B), and the metal powder (40C) are layered in turn in the die in the step of filling and layering the powders, and

the layered compact of the powders are integrally compacted in the step of compacting.

28. The production method for a thermal stress relief pad for thermoelectric conversion elements according to claim 25,

wherein the mixed powder (40B) and the electrical insulating material powder (40A) are layered in turn in the die in the step of filling and layering powders, or

the metal powder (40C), the mixed powder (40B) and the electrical insulating material powder (40A) are layered in turn in the die in the step of filling and layering powders,

the layered compact of the powders are integrally compacted in the step of compacting, whereby two green compacts are obtained, and

the green compacts are sintered in a state in which surfaces of layers of the electrical insulating material powder (40A) are contacted to each other in the sintering step, thereby being connected.

29. The production method for a thermal stress relief pad for thermoelectric conversion elements according to claim 25, wherein

the electrical insulating material powder (40A) includes at least one binder selected from a group consisting of methyl cellulose (MC), polyvinyl alcohol (PVA), ammonium alginate acid, carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), and polyvinyl pyrrolidone (PVP),

wherein the binding agent is mixed in a ratio of not more than 1 mass %.

30. The production method for a thermal stress relief pad for thermoelectric conversion elements according to claim 25, wherein

the binder is mixed into the electrical insulating material powder (40A) in a middle portion layer in a thickness direction, and

the mixed powder is granulated so as to have a particle diameter of not more than 150 μm.

31. The production method for a thermal stress relief pad for thermoelectric conversion elements according to claim 25,

wherein the mixed powder (40B) has two or more mixed powders which have different composition from each other,
wherein the metal powder (40C) is mixed in a volume not less than that of the electrical insulating material powder (40A) on the side of the metal layer formed on an end face, and

the electrical insulating material powder (40A) is mixed in a volume more than that of the metal powder (40C) in a electrical insulating layer formed at a middle portion in a thickness direction.

32. A production method for a thermal stress relief pad for thermoelectric conversion elements, comprising steps of:

filling a mixed powder (40B) of a metal powder and an electrical insulating material powder in a die, or

filling and layering a mixed powder (40B) of a metal powder and an electrical insulating material powder, and a metal powder (40C) in turn in a die;

forming a green compact of the layered powders by compacting the layered powders, whereby two green compacts of the layered powders are obtained;

coating an electrical insulating material powder (40A) on a surface of a layer of the mixed powder (40B) of one of the green compacts; and

connecting the green compacts via the electrical insulating material powder (40A) by sintering.

33. The production method for a thermal stress relief pad for thermoelectric conversion elements, according to claim 32,

wherein the electrical insulating material powder (40A) coated on a surface of a layer of the mixed powder (40B) is dispersed in a liquid so as to be made into slurry.

34. The production method for a thermal stress relief pad for thermoelectric conversion elements according to claim 32,

wherein the mixed powder (40B) has two or more mixed powders which have different composition from each other,

wherein the metal powder (40C) is mixed in a volume not less than that of the electrical insulating material powder (40A) on the side of the metal layer formed on an end face, and

the electrical insulating material powder (40A) is mixed in a volume more than that of the metal powder (40C) in an electrical insulating layer formed at a middle portion in a thickness direction.