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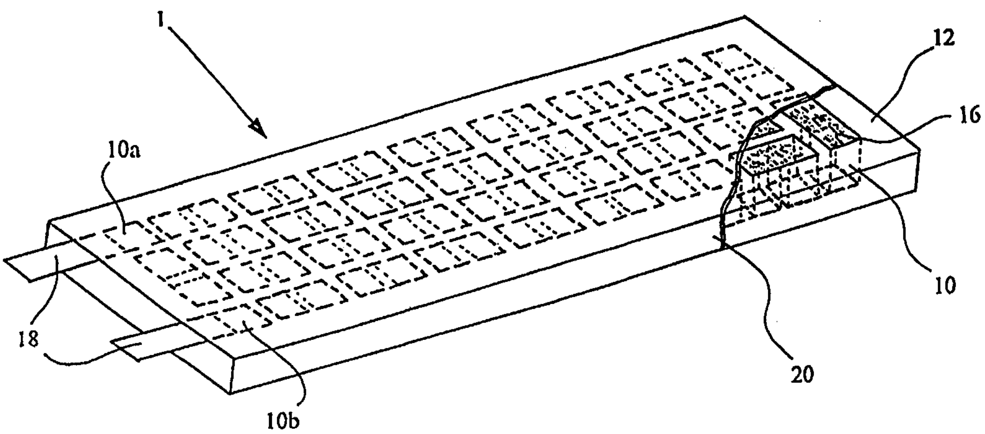

(57) Abstract

A thermoelectric device (1), and a method for manufacturing said device (1), intended for high–temperature applications for converting heat to electricity by means of the Seebeck effect. The device (1) consists of a green body sintered in protective atmosphere, which in turn consists of a body (12) of hardened ceramic material with thermoelectric couples (10) embedded therein. The ceramic material of the body shows a significantly increased porosity, which has been obtained by means of pore–forming means, preferably microballoons or microspheres (13), admixed to the ceramic material. Conduction paths (16) for connection of the thermoelectric couples (10) consist of thermally sprayed, electrically conductive contact material. This contact material is sprayed onto the end surfaces of the couples (10) and onto surfaces of the body (12) which are positioned between the thermoelectric couples (10) that are to be connected.

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THERMOELECTRIC DEVICE

Field of the Invention

The present invention relates to a thermoelectric device intended for high-temperature applications and adapted to convert heat to electricity by means of the Seebeck effect, a method for manufacturing the device, and a method for contacting thermoelectric couples included in the device.

Background Art

There is in many contexts a need for converting heat to electricity. A field involving specific kinds of need is high-temperature applications, i.e. applications in temperature ranges typically from about 400° and higher. Such applications can include the recovery of excess heat, for instance, in process industries, from heat pumps or from internal combustion engines and exhaust gas catalysts in vehicles. Further examples may comprise the recovery of frictional heat from, for example, brakes.

This can be achieved thanks to the Seebeck effect, i.e. a thermoelectric effect which means that voltage arises in an electric circuit composed of two different metals if the two contact points where the metals meet have different temperatures; in other words, devices utilising the Seebeck effect have a hot side and an opposite cold side. With a semiconductor material, a relatively high voltage can be achieved in this way, and by connecting in series a plurality of semiconductor elements of alternatingly p type and n type, voltages of several tens of volts can be obtained.

A typical thermoelectric device for use in said high-temperature range is disclosed in US Patent Specification US-A-4,459,428 (Chou). This specification discloses a thermoelectric device for generating electricity, comprising parallel, rod-shaped, n- and p-doped thermoelectric couples connected in series and arranged between two separate sets of copper segments and attached thereto by using soldering paste screen-printed on the inner surfaces of the sets of copper segments. The space between the thermoelectric couples and the copper segments is filled with a ceramic moulded mass, and the outer surfaces of the device are covered with a ceramic thick film insulator. A device of this type, however, has been found unsatisfactory.

Objects of and Summary of the Invention

An object of the present invention is to provide a new and improved thermoelectric device intended for high-temperature applications.

It is also an object of the present invention to provide a thermoelectric device having a reduced sensitivity to thermal expansion.

A further object of the present invention is to provide a simple method for manufacturing a thermoelectric device as stated above, which requires only a few heat treatments.

One more object of the present invention is to provide simpler contacting, i.e. mutual connection and external connection of thermoelectric couples in a thermoelectric device stated above.

These and other objects are achieved by a device and methods having the features which are defined in the appended claims.

According to a first aspect of the present invention, a thermoelectric device is provided, which is intended for high-temperature applications and comprises thermoelectric couples in a body of ceramic material, wherein the ceramic material, at least partially, has been given a significantly increased porosity, preferably exceeding about 30%, more preferred exceeding about 60%.

According to a second aspect of the present invention, a thermoelectric device is provided, which is intended for high-temperature applications and comprises thermoelectric couples in a body of ceramic material, wherein conduction paths for mutual electric connection and preparation for external electric connection of the thermoelectric couples consist of electrically conductive contact material thermally sprayed on the end surfaces of said thermoelectric couples and on surfaces of the body which are positioned between the thermoelectric couples that are to be connected.

According to a third aspect of the present invention, a method is provided for manufacturing a thermoelectric device intended for high-temperature applications, comprising the steps of making a green body with a body of hardened ceramic material with thermoelectric couples embedded therein; heat-treating the green body; and electrically contacting the thermoelectric couples for forming conduction paths.

According to a fourth aspect of the present invention, a method is provided for forming conduction paths for mutual electric connection of the end surfaces of thermoelectric couples in a thermoelectric device, comprising said thermoelectric couples arranged in, preferably cast into, a body of ceramic material, wherein the conduction paths are formed by thermal spraying of electrically conductive material on the end surfaces of the thermoelectric couples and on surfaces of the body which are located between the thermoelectric couples that are to be mutually connected.

A fifth aspect of the present invention involves use of microballoons or microspheres for forming, in a thermoelectric device comprising thermoelectric couples in a body of ceramic material, a heat-insulation-increasing porosity of the ceramic material.

A sixth aspect of the present invention involves use of microballoons or microspheres in combination with a binder, preferably an enamel, for adapting, in a thermoelectric device comprising thermoelectric couples in a body of ceramic material, the coefficient of thermal expansion of the ceramic material to the coefficient of thermal expansion of the thermoelectric couples which are arranged in, preferably cast into, the body.

These aspects of the invention can, as a person skilled in the art realises, be combined in an arbitrary manner without deviating from the inventive concept.

According to an embodiment, the invention relates to a thermoelectric device comprising thermoelectric couples, preferably p- and n-doped semiconductor elements, below referred to as thermocouples, in a body of ceramic material, the thermocouples being cast into the ceramic material so that the thermocouples together with the body constitute a uniformly composed body, on which the requisite conduction paths can be formed by means of applied conductive layers. This gives, among other things, the advantage that the device consists of a small number of components and that the manufacture will be simple in respect of process technology. The device comprises no loose parts, which improves its durability and facilitates handling. It is also easy to obtain the desired porosity of the ceramic body.

It has been found advantageous to carry out the casting of the ceramic body round the thermocouples in such manner that in the resulting uniformly composed body both end surfaces of each thermocouple are uncovered on opposite sides of said body. This means that contacting, i.e. mutual connection and preparation for external electric connection of the thermocouples, can be easily effected after casting. This simplifies the method of manufacture and makes it more efficient. Alternatively, the thermocouples can already be contacted in the casting of the body.

According to the invention, the method of manufacture is made still more efficient owing to the fact that the thermocouples, before being cast into the body, are not finally heat treated but consist of blanks, so-called green elements. This means that the final heat treatment of the thermocouples is carried out after they have been cast into the above-mentioned uniformly composed body, i.e. in connection with the heat treatment of the body. In other words, the body and the thermocouples are finally heat-treated simultaneously, which reduces the number of necessary heat treatments. Simultaneous heat treatment of the thermocouples and the body is facilitated if the thermocouples and the selected ceramic material have at least practically the same coefficient of thermal expansion while taking the porosity of the ceramic material into consideration.

As mentioned above, it has according to the invention surprisingly been found that it is possible to affect in an advantageous manner the coefficient of thermal expansion of the ceramic body material by admixing, before the casting of the body, microballoons (or microspheres) together with a binder, preferably an enamel, to the ceramic slurry which is used for casting the body. This yields a possibility of adapting the coefficient of thermal expansion of the ceramic material to that of the thermocouples, preferably owing to the selection of the binder that is to be admixed to the ceramic material. Consequently no tension arises between the ceramic material and the thermocouples when the device is exposed to high temperatures, which tension could result in cracking and, if the worst comes to the worst, the device being useless.

As mentioned above, it is according to the invention also possible to affect the thermal conductivity in the thermoelectric device by forming a porosity in the ceramic material. According to a preferred embodiment of the invention, said porosity can be produced by admixing microspheres or microballoons to the ceramic body material. The microballoons have a closed outer surface but a hollow interior so that small well-defined and well-distributed voids or pores form in the ceramic material.

By admixing microballoons, the heat insulating capacity of the body, and thus of the entire device, increases. This contributes positively to the thermoelectric effect since a greater difference in temperature across the device can be maintained, which in turn results in the possibility of obtaining a higher output voltage and a higher current intensity. Moreover a higher porosity allows quicker heating and cooling during the heat treatment in the manufacture.

It has been found advantageous, in the contacting of the device, to have a higher thermal conductivity in the body portion closest to the surface that is to be contacted. This gives the advantage of improved removal of heat in contacting by thermal spraying (as will be described below) of conduction paths. According to an embodiment of the invention, a surface layer of the body is therefore given a significantly lower porosity than the rest of the body, preferably by this surface layer being produced at least essentially without admixing microballoons. This also results in greater strength of this surface layer, which allows that the amount of microballoons in an inner layer enclosed by the surface layer can be increased, which further increases the thermoelectric effect.

The above-mentioned microballoons may consist of, for instance, balloons of glass, foamed aluminium oxide or some other foamed ceramic material, such as silicon dioxide (SiO_2) or zirconium dioxide (ZrO_2). The diameter of the microballoons can typically be between 10 and 250 μm, preferably about 150 μm.

As mentioned above, it is advantageous that the body of ceramic material and the thermocouples cast into the same are not finally heat-treated but consist of a so-called green body. To achieve a strength which is sufficient for the green body for the final heat treatment, which may consist of, for instance, sintering, a number of methods can be used. Such a method comprises the adding of cement to the ceramic slurry, from which the body is to be cast, so that the green body hardens hydraulically to sufficient hardness. This method results in a very strong ceramic body. A further method comprises adding starch or a similar organic material to the ceramic slurry together with, alternatively instead of, said cement. After having poured this slurry into a mould for casting of the ceramic body, heating takes place, for instance to about 80°C, in which heating the starch absorbs water and acts as a glue in the green body. In a subsequent final heat treatment at a higher temperature, for instance sintering, the starch is gasified and forms pores in the ceramic. An advantage of using starch is that the pores formed further increase the porosity of the body with the ensuing positive effects, as described above. However, the use of cement results in a somewhat stronger green body.

According to an alternative preferred embodiment of the invention, the ceramic body-forming material consists of an aluminium orthophosphate (AlH_2PO_4). Since the hardened aluminium orthophosphate, also after the admixing of microballoons, has an inherent elasticity, no adaptation of the coefficient of thermal expansion of the body to that of the thermocouples is required. Moreover, the requisite binding between the aluminium orthophosphate and the microballoons is obtained without adding a binder, thus eliminating the need for a binder, which in turn results in the final heat treatment requiring a substantially lower temperature. A final heat treatment at a temperature of about 100-400°C, preferably at about 150-200°C, is sufficient, i.e. no sintering of the green body is necessary. This also eliminates the need for adding cement or starch to the slurry to obtain the required strength prior to sintering. This facilitates the process of manufacture to a considerable extent, inter alia, by the time needed for hydraulic hardening being eliminated.

With a view to obtaining improved binding in the body, it has according to the invention also been found advantageous to add, in connection with the admixing of the microspheres to the slurry, an agent which reduces the surface tension of the aluminium orthophosphate solution that is included in the slurry. Owing to the fact that the surface-tension-reducing agent also reduces the viscosity of the slurry, the requisite stirring time is reduced to a very great extent. This results in turn in a great reduction of the risk that the microspheres are crushed during stirring. The surface-tension- and viscosity-reducing agent can be, for instance, ethanol.

The contacting of a device according to the invention can in fact be carried out in different ways, for example by screen printing of conductive patterns, electrolytic precipitation, soldering etc. According to the invention, however, it has been found advantageous for the contacting to apply a conductive material by thermal spraying or what is referred to as sputtering, in which case the conductive material is deposited directly on the body containing the thermocouples, i.e. in the preferred case on the ceramic body material and the end surfaces of the thermocouples, and forms conduction paths in the form of layers. This results in, besides simple and inexpensive contacting, the possibility of making the applied conduction layers very thin. It has also been found that thermally sprayed layers have the advantage of possessing a certain inherent possibility of moving. This reduces the risk of cracking and the like in case of motions owing to tension arising because of heat changes.

A number of metals yield excellent conductivity and are well suited for said contacting, such as copper and gold. An advantage of using copper is that contact elements of copper for external connection of the device can easily be fastened, for instance by spot welding. However, a problem with many of these metals, including copper, is that they can react with thermocouples which are semiconductor elements and deteriorate or destroy these. Moreover, a high transition resistance between thermocouples of said type and the metal is obtained, which decreases the thermoelectric effect of the device. According to the invention, these problems are solved by first applying, preferably by sputtering or thermal spraying, at least to the end surfaces of the thermocouples a thin barrier or transition layer of a conductive material compatible with the semiconductor material, preferably tin-telluride (Sn-Te) on the hot side and nickel-antimony (Ni-Sb) or tin-telluride on the cold side. Such a layer also results in a low transition resistance to both the thermocouples and the metal. Other examples of suitable materials for this layer can be molybdenum (Mo), nickel (Ni), iron (Fe) or a mixture of nickel and aluminium (Ni-Al).

According to the invention, it has been found advantageous to apply said first layer only to the end surfaces of the thermocouples, that is not on the ceramic body material, which makes it possible to apply the first thin barrier and transition layer even before the casting of the thermocouples into the body. This allows in itself that a large number of thermocouples, in the present case even exceeding the number of thermocouples contained in a thermoelectric device, can at the same time be provided with said barrier layer, which renders manufacture more efficient. If the application of the barrier layer takes place prior to casting, it is preferably carried out by means of sputtering.

After the forming of said uniformly composed body which on the end surfaces of the thermocouples has been provided with the applied first layer, the metal, which preferably is copper, is applied by spraying to obtain the desired conduction paths. Although the conductive material compatible with the semiconductor material has a conductivity inferior to that of, for instance, copper, the total conductivity is affected to a very small extent owing to the fact that the first applied barrier layer can be made very thin. The actual contacting pattern can be formed, for instance, by direct layer-pattern-controlled spraying or by spraying through a template or mask arranged across the uniformly composed body.

The thermal contacting spraying may consist of, for instance, plasma spraying, arc spraying, wire spraying or powder spraying. According to a preferred embodiment of the invention, the thermal spraying consists of high-velocity flame spraying (VHOF), which produces a higher density of the sprayed-on contacting layers and, thus, improved electric properties.

According to an alternative embodiment of the invention, the conductive layer may consist of iron, in which case no separate barrier layer is necessary. Furthermore iron is well suited for thermal spraying. Since iron is a conductor inferior to, for example, copper, it is, however, necessary for a much thicker contacting layer of iron to be applied than is necessary with copper, which increases the weight and the extent of the device.

The sensitivity of the semiconductor material to reaction with abutting contacting metals is heat dependent, i.e. the semiconductor material is more sensitive at higher temperatures. At a sufficiently low temperature, it has been found that this sensitivity is negligible. According to the invention, this can be utilised by a barrier layer advantageously not being applied to the semiconductor element end surfaces which are positioned on the cold side. It will be appreciated, however, that this embodiment of the invention can only be used in the cases where one wants to ensure that the temperature on the cold side of the device can continuously be kept sufficiently low, typically below 100°C.

The size, appearance and number of the thermocouples may vary according to the application involved. According to the invention it has been found advantageous that the thermocouples have a typical length of between 5 and

15 mm, preferably about 8 mm, and a typical area of between 10 and 25 mm^2, preferably about 20 mm^2. The thermocouples are not bound to a certain shape. However, it has been found advantageous to have the shape of a parallelepiped or cylinder, which gives the thermocouples square or circular end surfaces.

The number of thermocouples is adapted to the desired output voltage. The output voltage that can be obtained for each thermocouple is typically 0.3 V, which is multiplied by the number of thermocouples connected in series so as to obtain the desired output voltage. According to a preferred embodiment, an output voltage of about 14 V is desired, which requires 48 thermocouples connected in series. It goes without saying that higher as well as lower output voltages can be obtained. Nor is the invention restricted to connecting the thermocouples in series, as a person skilled in the art will realise, but also other connections can be used, such as connecting in parallel or combinations of connecting in parallel and in series. Of course, this is adapted to the selected application.

The completed device can be seen as a module which in itself can be connected in series and in parallel with similar modules.

With a view to protecting the device from being damaged on the outside and providing electric insulation of the device, there is preferably applied an outer protective casing which surrounds the body and the thermocouples arranged therein and, arranged thereon, contacting conduction paths. This casing can preferably consist of a layer of ceramic material, preferably an enamel. According to the invention, it has been found advantageous to apply this layer by thermal spraying, preferably by plasma spraying. This facilitates the process of manufacture still more. This layer can also be applied by, for example, wet spraying.

Moreover, according to a preferred embodiment of the invention, it has been found advantageous to apply, on the outside of the above-mentioned protective layer, a further protective layer of a mixture of yttrium (Y) and zirconium dioxide (ZrO_2), for example by thermal spraying. This results in an increase of the strength of the device as well as a more uniform temperature distribution over the hot and the cold side of the device.

The invention will now be described in more detail by way of exemplifying embodiments with reference to the accompanying drawings.

Brief Description of the Drawings

Fig. 1 is a schematic perspective view of a device according to a preferred embodiment of the invention;

Figs 2-7 illustrate schematically the steps included in a method for manufacturing the device in Fig. 1, according to a preferred embodiment of the invention;

Fig. 8 is a schematic part-sectional view, and an enlarged portion thereof, of the device according to Fig. 1;

Fig. 9 is a schematic part-sectional view, and an enlarged portion thereof, of a device according to an alternative embodiment of the invention; and

Fig. 10 is a schematic part-sectional view of a further alternative embodiment of the invention.

Detailed Description of Preferred Embodiments

A preferred embodiment of a device according to the invention will now be described with special reference to Figs 1 and 8.

The thermoelectric device 1 is intended for conversion at high temperature of heat to electricity by the Seebeck effect. The device 1 consists of an elongate, plate-shaped uniformly composed body or module with two contact elements 18 projecting from the body. The two opposite sides of the device 1 having the largest area constitute the so-called hot and the cold side of the device 1. The surface on the hot side is adapted to abut against a source of heat, for example a catalyst or a car engine, and the surface on the cold side is adapted to abut against a cooling element, which, for example, is connected to the cooling system of a car. The device 1 comprises a number of n-doped and p-doped thermoelectric semiconductor elements 10, below referred to as thermocouples, arranged in parallel rows. The n-doped and p-doped thermocouples 10 are alternatingly connected in series, i.e. each p-doped thermocouple is connected in series with two neighbouring n-doped thermocouples and vice versa, one connection to a neighbouring thermocouple being arranged on the cold side of thermocouple and the other on the hot side of the thermocouple, except the first 10a and the last 10b thermocouple in the series. These two thermocouples are connected to contact elements 18 for external contacting of the device 1. The thermocouples 10 are formed as elongate parallelepipeds with rectangular end surfaces.

The thermocouples 10 are cast into a body 12 which, according to a first embodiment, consists of a ceramic material, an enamel, a binder and microballoons or microspheres 13 embedded and distributed in the body 12; and according to a second embodiment, of a ceramic material and microballoons or microspheres 13. The thermocouples 10 extend between opposite sides of the body 12 so that the end surfaces of thermocouples 10 are not covered by the body 12 and form, together with the opposite sides of the body 12, two opposite even surfaces.

On the hot and the cold side of the device, the end surfaces of the thermocouples 10 are provided with a first, sputtered, very thin and electrically conductive inner layer 14 as described above. The material of this inner layer 14 is compatible with the material of which the thermocouples 10 are made and therefore constitutes a so-called barrier layer or transition layer between the thermocouples 10 and further contacting layers. Thanks to the sputtering, the first layer 14 can be made very thin.

On the barrier layer 14 and on the surface of the body 12 which is positioned between the thermocouples 10 that are to be interconnected, there is applied a second high velocity flame sprayed outer contacting layer 16 of a material which yields excellent electric conduction between the thermocouples 10. The outer contacting layer 16 is somewhat thicker than the barrier layer 14 and is responsible for the electric conduction between the thermocouples 10. The contacting layer 16 forms the elongate conduction paths which connect the thermocouples 10 in series.

In one end of the device 1, on its cold side, there are arranged two elongate, rectangular contact elements of sheet metal 18 mentioned by way of introduction. The contact elements 18 are at one end 18a fixed to the first and the last thermocouple 10a, 10b connected in series and project therefrom in parallel with the end surfaces of the thermocouples 10 in the longitudinal direction of the device 1 in such manner that the contact elements 18 at their other end 18b project beyond the actual device. The contact elements 18 are at said one end 18a point welded to the respective thermocouples 10a, 10b and are intended for external electric connection of the device 1.

The device 1 is further enclosed by a wet-sprayed, sintered electrically insulating protective layer 20. However, the parts 18b of the contact elements 18 which project from the body of the device are not provided with any further coating.

Finally and as an alternative, the device 1 can be provided with one more powder-sprayed protective layer 22. The layer 22 is arranged to yield on the one hand reinforcement of the device 1 and, on the other hand, a more uniform temperature distribution across the hot and the cold side of the device 1. This embodiment is illustrated in Fig. 9.

Next follows a description of a typical example of the dimensioning and the material selected for the device according to the preferred embodiment described above. The device 1 assumes the shape of a parallelepiped having the approximate dimensions 120 x 40 x 10 mm, the contact elements 18 projecting from the body being excluded. The thermocouples 10 have a length of 8 mm and the rectangular end surfaces have the dimensions 4 x 5 mm. The material of the thermocouples 10 is lead-telluride with dopes added. The rectangular contact elements 18 which are arranged for external connection of the device are made of copper.

According to a first embodiment, the body 12 consists of a ceramic material, alumina or aluminium oxide (Al_2O_3); a cement, calcium aluminate ($3CaO \cdot Al_2O_3$); an enamel, 94C1001 Plux supplied by Cookson Matthew Ceramics; and microballoons 13, Fillite 150 supplied by Astmoor Industrial Estate, Sil-cell 140 supplied by Stauss Gesellschaft. According to a second embodiment, the body 12 is made of a ceramic material, aluminium orthophosphate (AlH_2PO_4); and microballoons 13, Eccospheres supplied by Emerson & Cuming Inc. The material of the barrier layer 14 is on the hot side tin-telluride (Sn-Te) and on the cold side nickel-antimony (Ni-Sb), which materials are compatible with the lead-telluride of which the thermocouples 10 are made. The material of the outer contacting layer 16 is copper. The barrier layer 14 has a thickness of about 5 μm and the outer contacting layer 16 has a thickness of about 100 μm.

The material of the protective, insulating, wet-sprayed layer 20 is an enamel, more specifically 94C1001 Plux supplied by Cookson Matthew Ceramics. The optionally additionally applied protective layer 22 is of zirconium dioxide (ZrO_2), which yields the properties that have been described above.

Fig. 10 illustrates an alternative embodiment of the invention. According to this embodiment, the body 12 is made in two layers with different porosity, an inner layer 12a between two outer layers 12b. The outer layers 12b and the inner layer 12a together form a body which is to the other components as is the uniformly composed body 12 in the manner described above. The surface layers 12b typically have a thickness of 0.5 mm and have no admixed microballoons at all. The inner layer 12a may comprise a larger amount of microballoons 13 than in the case of the body 12 according to the above-mentioned preferred embodiment.

Below follows a description of a preferred embodiment of a method according to the invention with special reference to Figs 2-9.

A first part 31 of a mould is provided with a self-adhering surface 34 which is obtained by means of a piece of adhesive tape. On this surface, a number of n-doped and p-doped thermocouples 10 as described above are arranged in parallel rows and adhere to the tape, the thermocouples 10 being arranged successively so that every other thermocouple is n-doped and every other is p-doped. The thermocouples 10 consist of hot-pressed semiconductor elements containing a mixture of lead (Pb), tellurium (Te) and dopes which have been produced in a manner known per se, which will therefore not be described in more detail. However, the thermocouples 10 are not finally heat treated when they are placed in the first part 31 of the mould but constitute so-called green elements.

The thermocouples 10 are, when being arranged in the mould, provided on their end surfaces with a first barrier layer 14 which is applied by sputtering and which on the hot side is of tin-telluride and on the cold side of nickel-antimony.

A second part 32, the cover, of the mould, is arranged in liquid-tight connection with the first mould part 31 which at one end is formed with an aperture for pouring of casting composition 11. The parts of the mould together constitute a mould 30. The dimensions of the respective parts 31, 32 of the mould are such that the end surfaces of the thermocouples 10 abut in a liquid-tight manner against the inwardly directly surfaces of the parts 31, 32 of the mould. The mould 30 is then placed on its end, whereupon a casting composition 11 is poured into the mould 30 under vibration.

According to a first embodiment, the casting composition 11 is produced by mixing 55% C96 supplied by Höganäs, 20% calcium aluminate, 5% 94C1001 Plux supplied by Cookson Matthew Ceramics, all pulverulent, and 20% Fillite 150 supplied by Astmoor Industrial Estate. After careful mixing of the powders and the balloons, water is added so that a slurry having a thick consistency is obtained. This slurry consists of said casting composition 11 and is poured into the mould 30 provided with thermocouples 10. The casting composition 11 is then allowed to harden at room temperature to a ceramic body 12 containing the thermocouples 10 cast into the body 12.

After this hardening, the device is, according to said first embodiment, allowed to air-dry for at least 24 h. Now the device is as a so-called green body ready to be heat-treated, which takes place in a vacuum oven for 30 min, the pressure in the oven chamber being pumped down to 5 x 10^{-6} atmospheres. Subsequently the chamber as filled to atmospheric pressure with nitrogen (N_2) or argon (Ar) and is then heated to about 700°C; the heating time should be at least 1 h. This temperature is then kept for at least 30 min, whereupon cooling takes place in the oven when switched off.

According to a second embodiment, the casting composition is produced by mixing 2/3 of aluminium orthophosphate solution (e.g. 48% AlH_2PO_4, MAP, supplied by Albright & Wilson U.K. Ltd.) and 1/3 of silicon dioxide spheres (e.g. Eccospheres supplied by Emerson & Cuming

Inc.) in the size range 30-180 μm. Moreover, ethanol is added to reduce the viscosity and, thus, the time of stirring, as well as the surface tension of the aluminium orthophosphate solution, and thus improve the binding between the microballoons and the aluminium orthophosphate. This slurry is stirred for about 3 min and then constitutes the casting composition 11 which is poured into the mould 30. The casting composition 11 is then allowed to harden in a drying cabinet at 40°C for about twelve hours. Then the temperature in the drying cabinet is raised to 80°C, and the casting composition is allowed to harden for approximately five more hours.

After this hardening, the device is now, according to said second embodiment, as so-called green body ready for heat treatment. This heat treatment is carried out in an oven, at room atmosphere and at atmospheric pressure, at about 200°C for about three hours.

The next step is to provide the device 1 with conduction paths 16 for mutual electric connecting in series of the thermocouples 10 and for external connection of the device 1 by means of the first and the last thermocouple 10a, 10b contained in the connection in series. This is carried out by arranging masks or templates 36 on the cold and the hot side of the device 1. The masks 36 are formed with rectangular holes and after being arranged on the device 1, each hole encircles end surfaces of two neighbouring thermocouples 10, one being p-doped and the other n-doped, and also the intermediate surface of the body 12 so that the thermocouples can be connected in series. For the two thermocouples 10a, 10b whose end surfaces are intended to constitute the first and the last end surface of said connection in series, the corresponding holes in the mask 36 which is to be arranged on this side are designed so that only said first and said last end surface are encircled by each hole.

An outer contacting layer 16 of copper is then applied to the encircled surfaces, i.e. to the respective barrier layers 14 and to the surface of the body which is located between the thermocouples that are to be interconnected. The layer 16 is applied through the masks 36 by high velocity flame spraying (HVOF). The inner layer 14 thus constitutes a barrier or transition layer which on the one hand protects the end surfaces of the thermocouples 10 from being toxically affected by the outer layer 16 and, on the other hand, reduces the transition resistance between the thermocouples 10 and the copper layer 16. After applying the copper layer 16 and removal of the masks 36, the layer 16 constitutes conduction paths for mutual electric connection of the end surfaces of the thermocouples 10. The conduction paths 16 can be best seen in Fig. 7. The thermocouples 10 contained in the device 1 are now connected in series with the copper-layer-coated end surfaces of the first and the last thermocouple 10a, 10b, said end surfaces being arranged on the cold side of one end of the device.

The spraying is schematically illustrated in Fig. 6 and the application of layers by surface coating using HVOF is carried out in the following steps:

A powder of the material that is to be applied is supplied to a HVOF spray gun; the powder is mixed with a carrier gas supplied to the gun and is carried by the carrier gas to a nozzle; at the outlet of the nozzle a flame is produced by means of combustion gas supplied to the gun together with oxygen; the powder leaves the outlet of the nozzle at high speed, about 500 m/s, the powder melting as it passes through the flame and being sprayed in the form of molten droplets onto the object that is to be coated and forming a surface coating thereof.

External electric connection of the device 1 is then made possible by applying to the end surface of said first and said last thermocouple 10a, 10b an elongate, thin rectangular contact element 18 of copper. The two contact elements 18 are at their respective one end 10a welded to said end surfaces by spot welding. The contact elements 18 project from the respective thermocouples 10a, 10b perpendicular thereto in the longitudinal direction of the device 1 in parallel with the end surfaces of the thermocouples 10 so that the respective other ends 18b of the contact elements 18 project beyond the actual device, which is best seen in Fig. 7.

Next a protective, electrically insulating layer of enamel 20 is applied. The layer 20 is applied by wet spraying. The enamel layer 20 is applied in such manner that the entire device, including the body 12 and the thermocouples 10, together with the contacting layers 14, 16 are enclosed by the enamel layer 20. The parts of the contact elements 18 which project beyond the body 12 are not coated with enamel.

A final heat treatment of the device is effected by sintering in a furnace at about 700°C until the device has reached the same temperature as the furnace and then for about 10 min more. Cooling then takes place in the furnace when switched off. In this final heat treatment, enamelling of the enamel layer 20 is effected.

CLAIMS

1. A thermoelectric device (1) intended for high-temperature applications, comprising thermoelectric couples (10) in a body (12) of ceramic material, c h a r a c t e r i s e d in that the ceramic material, at least partially, has been given a significantly increased porosity, preferably exceeding about 30%, most preferred exceeding about 60%.

2. A thermoelectric device (1) as claimed in claim 1, wherein the porosity is obtained with the aid of pore-forming means admixed to the ceramic material, preferably microballoons or microspheres (13).

3. A thermoelectric device (1) as claimed in claim 2, wherein the ceramic material comprises a binder for the microballoons, preferably an enamel.

4. A thermoelectric device (1) as claimed in claim 2 or 3, wherein the ceramic material comprises a surface-tension- and viscosity-reducing agent.

5. A thermoelectric device (1) as claimed in any one of the preceding claims, wherein the body (12) of ceramic material together with the thermoelectric couples (10) forms a uniformly composed body without any further voids.

6. A thermoelectric device (1) as claimed in any one of the preceding claims, wherein the device comprises a hot and a cold side, and wherein the thermoelectric couples (10) are arranged in parallel and extend between the hot and the cold side of the body (12), the end surfaces of the thermocouples preferably being essentially on the same level as the surfaces of the body (12).

7. A thermoelectric device (1) as claimed in any one of the preceding claims, wherein conduction paths (16) for mutual electric connection and preparation for external electric connection of the end surfaces of the thermoelectric couples (10) consist of electrically conductive contact material thermally sprayed on the end surfaces and on surfaces of the body (12) which are positioned between the thermoelectric couples that are to be connected.

8. A thermoelectric device (1) as claimed in claim 7, wherein at least on the end surfaces of the thermoelectric couples (10) there is arranged an inner transition or barrier layer (14) of a contact material which is compatible with the thermoelectric couples (10).

9. A thermoelectric device (1) intended for high-temperature applications, comprising thermoelectric couples in a body (12) of ceramic material, c h a r a c t e r i s e d in that conduction paths (16) for mutual electric connection and preparation for external electric connection of the thermoelectric couples (10) consist of thermally sprayed, electrically conductive contact material on the end surfaces of the thermocouples (10) and on surfaces of the body (12) which are positioned between the thermoelectric couples that are to be connected.

10. A thermoelectric device (1) as claimed in claim 9, wherein at least on the end surfaces of the thermoelectric couples (10) there is arranged an inner transition or barrier layer (14) of a contact material which is compatible with the thermoelectric couples (10).

11. A thermoelectric device (1) as claimed in any one of the preceding claims, further comprising an electrically insulating layer (20) of ceramic material, pre-

ferably wet-sprayed enamel, surrounding the body (12), the thermocouples (10) and the conduction paths (16).

12. A thermoelectric device (1) as claimed in any one of the preceding claims, wherein the body (12) has a varying porosity.

13. A thermoelectric device (1) as claimed in claim 12, wherein the body (12) comprises surface layers (12b) having a significantly lower porosity, preferably about 10%, and an intermediate inner layer (12a) having a significantly higher porosity, preferably about 80%.

14. A method for manufacturing a thermoelectric device (1) intended for high-temperature applications, comprising the steps of

making a green body with a body (12) of hardened ceramic material with thermoelectric couples (10) embedded therein;

heat-treating the green body; and

electrically contacting the thermoelectric couples (10) for forming conduction paths (16).

15. A method as claimed in claim 14, wherein the heat treatment is carried out at about 100-400°C, preferably at about 150-200°C.

16. A method as claimed in claim 14, wherein the heat treatment consists of sintering, preferably in protective atmosphere.

17. A method as claimed in any one of claims 14-16, wherein the green body is made by the steps of

premounting thermoelectric couples (10) in a mould (30), the thermoelectric couples (10) themselves constituting so-called green elements;

filling the mould (30) with a hardenable slurry (11) of ceramic material;

hardening the slurry (11) so that the hardened slurry forms a body (12) which together with the thermoelectric couples (10) constitutes a uniformly composed body.

18. A method as claimed in claim 17, wherein the hardening is carried out at room temperature.

19. A method as claimed in claim 17 or 18, further comprising the step of

admixing pore-forming means to the slurry (11) of ceramic material prior to hardening.

20. A method as claimed in claim 19, wherein said pore-forming means consist of microballoons or microspheres (13).

21. A method as claimed in claim 20, wherein said microballoons or microspheres are admixed together with a binder, preferably an enamel.

22. A method as claimed in claim 20 or 21, wherein said microballoons or microspheres are admixed together with a surface-tension- and viscosity-reducing material.

23. A method as claimed in any one of claims 14-22, wherein the electric conduction paths (16) are formed by thermal spraying of electrically conductive contact material, which takes place after the sintering of the green body.

24. A method for forming conduction paths (16) for mutual electric connection of the end surfaces of thermoelectric couples (10) in a thermoelectric device (1), comprising said thermocouples (10) arranged in, preferably cast into, a body (12) of ceramic material,

characterised in that the conduction paths (16) are formed by thermal spraying of electrically conductive material on the end surfaces of the thermocouples (10) and on surfaces of the body (12) which are positioned between the thermoelectric couples that are to be connected.

25. A method as claimed in any one of claims 14-24, further comprising the step of

applying, at least to the end surfaces of the thermoelectric couples (10), prior to the forming of the conduction paths (16) an internal transition or barrier layer (14) of a contact material which is compatible with the thermoelectric couples (10).

26. A method as claimed in claim 25, wherein the barrier or transition layer (14) is applied to the end surfaces of the thermocouples (10) prior to the making of the green body.

27. A method as claimed in claim 25 or 26, wherein the barrier or transition layer (14) is formed by sputtering.

28. Use of microballoons or microspheres for forming, in a thermoelectric device (1) comprising thermoelectric couples (10) in a body (12) of ceramic material, a heat-insulation-increasing porosity of the ceramic material.

29. Use of microballoons or microspheres in combination with a binder, preferably an enamel, for adapting, in a thermoelectric device (1) comprising thermoelectric couples (10) in a body (12) of ceramic material, the coefficient of thermal expansion of the ceramic material to the coefficient of thermal expansion of the thermo-

couples (10) which are arranged in, preferably cast into, the body (12).

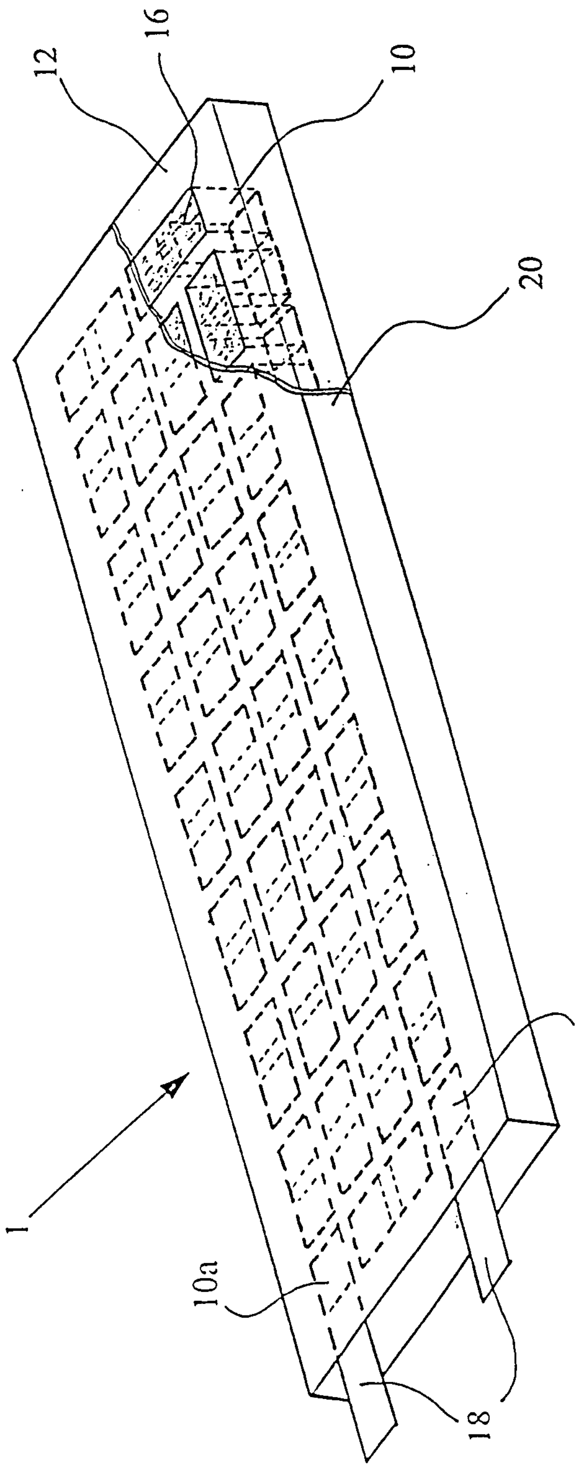

Fig. 1

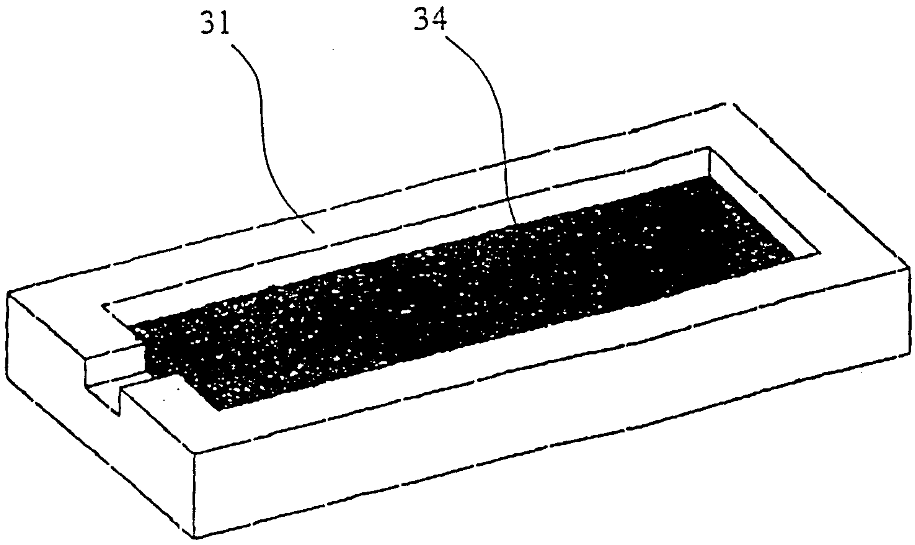

Fig. 2

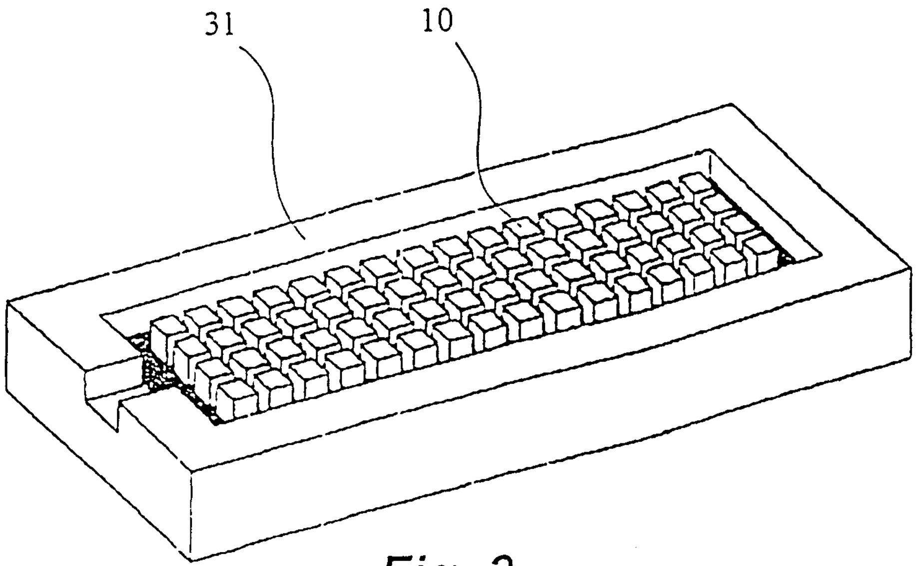

Fig. 3

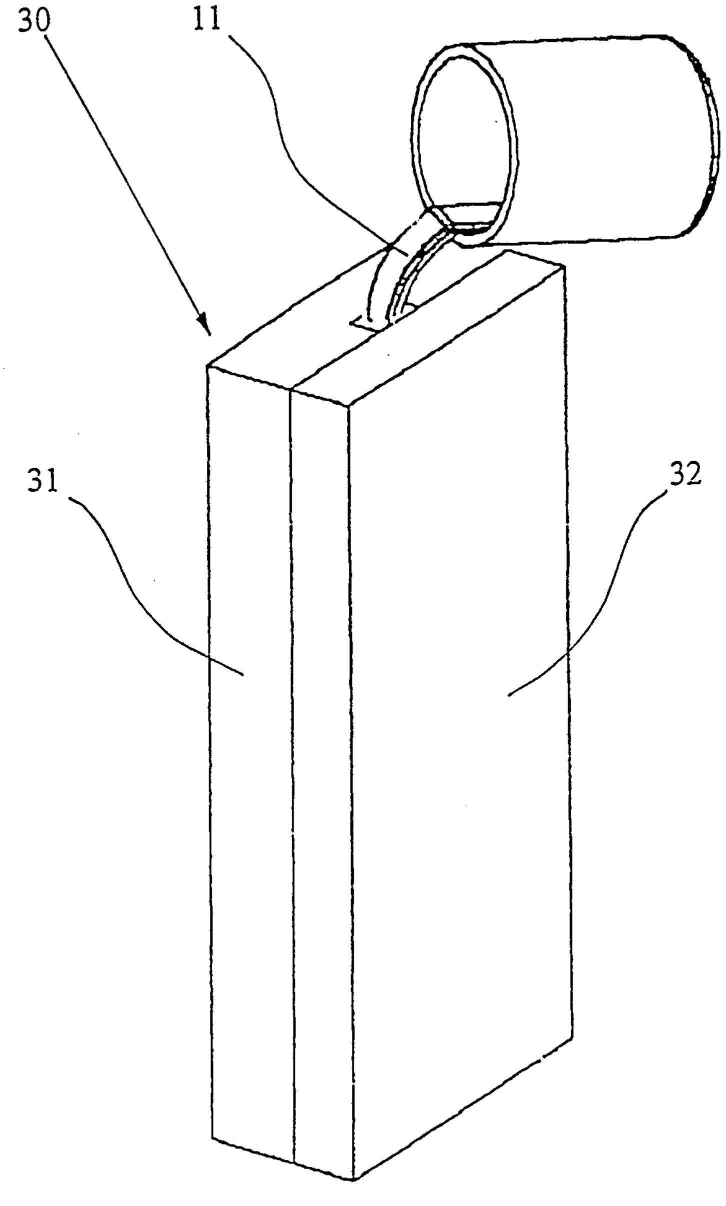

Fig. 4

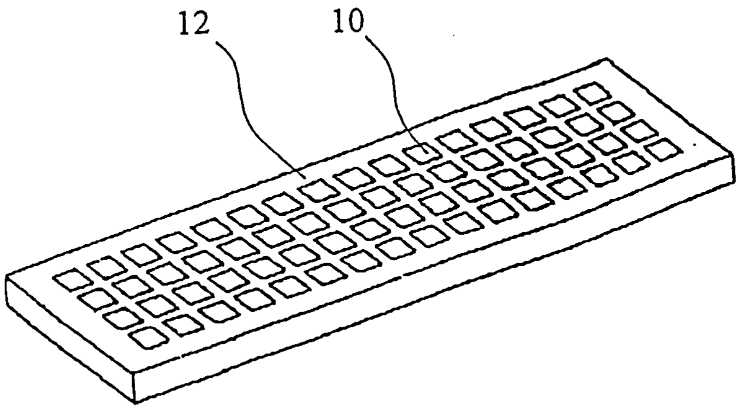

Fig. 5

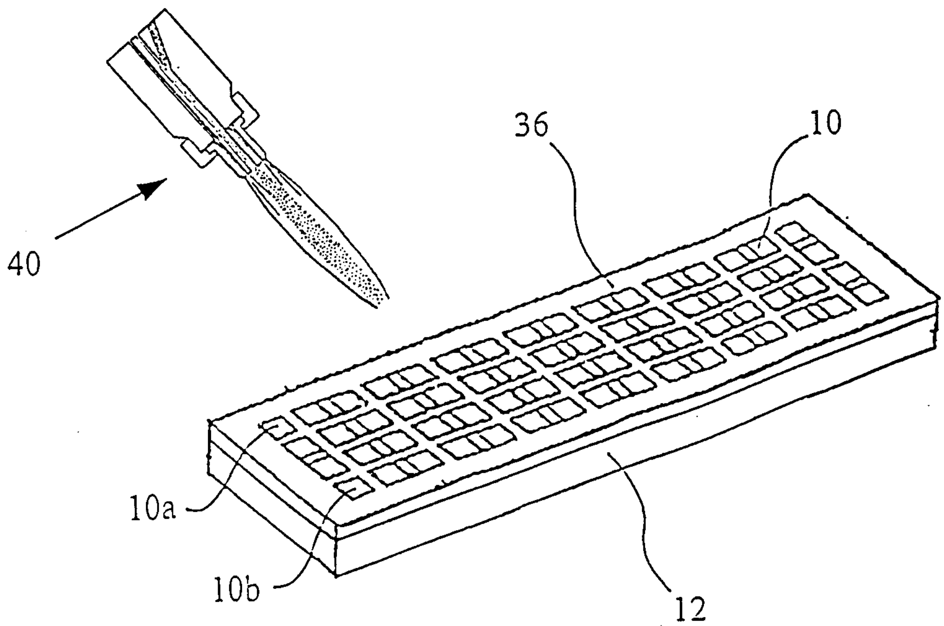

Fig. 6

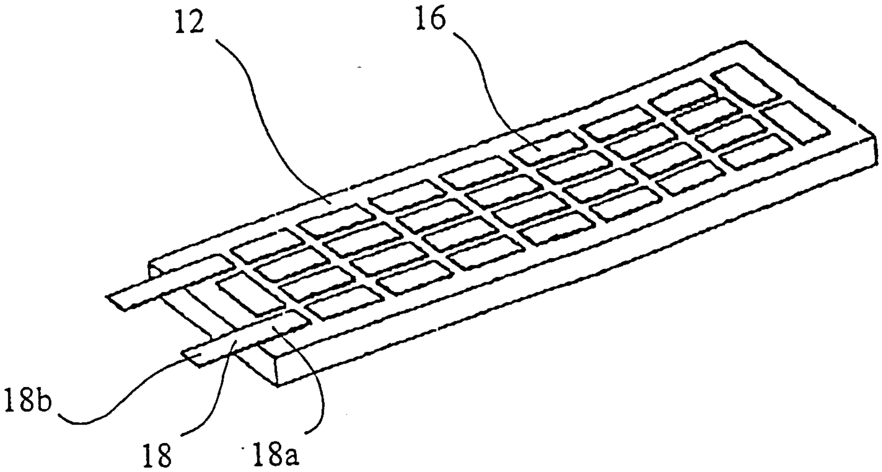

Fig. 7

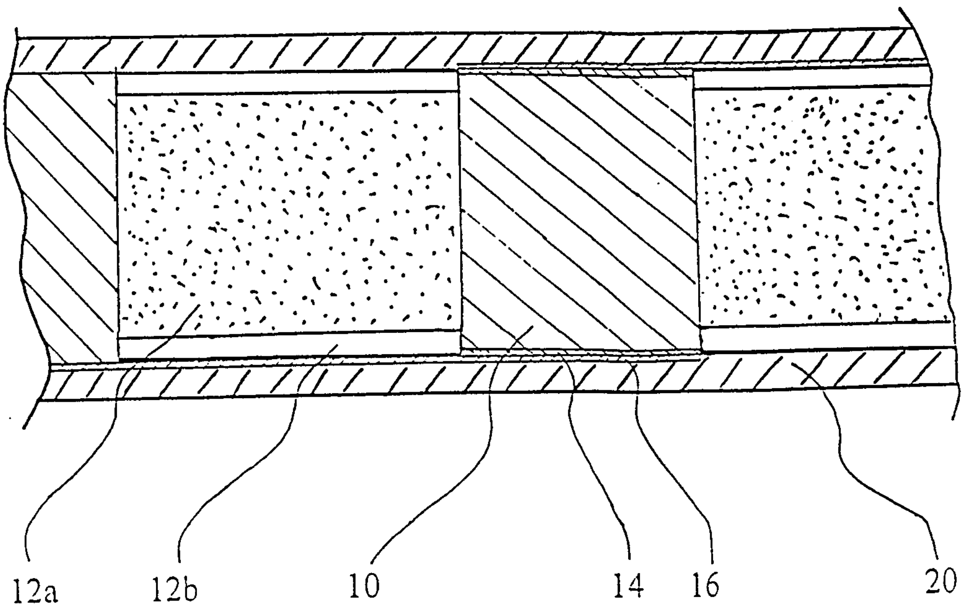

Fig. 10

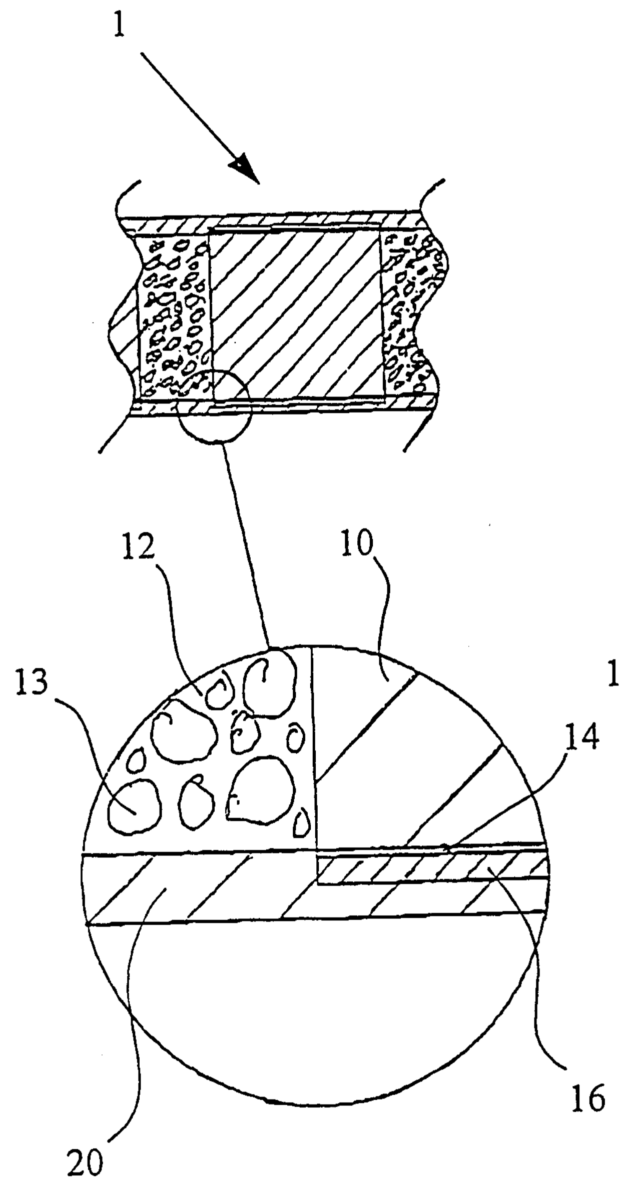

Fig. 8

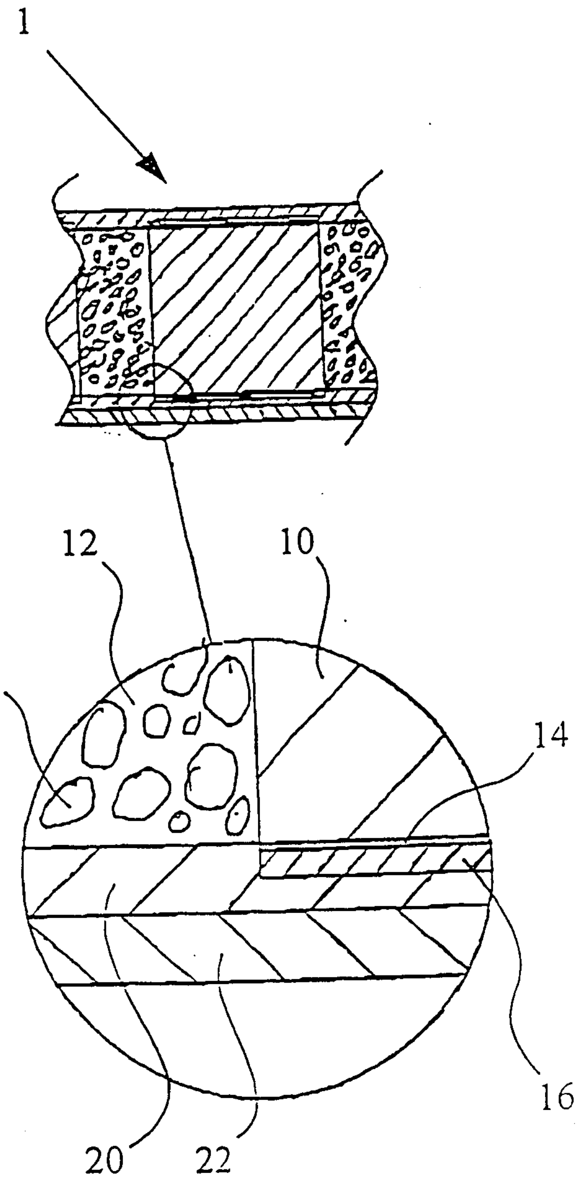

Fig. 9