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Thermoelectric Generator and Method
for the Fabrication Thereof

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THERMOELECTRIC GENERATOR AND METHOD FOR THE FABRICATION THEREOF

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DISCLAIMER

DISCLAIMER

CONTRACTUAL ORIGIN OF THE INVENTION

The United States Government has rights in this invention pursuant to Contract No. DE-AC02-83CH1 0093 between the U.S. Department of Energy and THE SOLAR ENERGY RESEARCH INSTITUTE, A DIVISION OF MIDWEST RESEARCH INSTITUTE.

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

This invention relates to the field of thermoelectric generators and in particular to thermoelectric generators utilizing thin film thermoelectric alloys on selected substrates.

2. DESCRIPTION OF THE PRIOR ART

Thermoelectric generators have been known for several years. One of the problems associated with thermoelectric generators is in relation to the relatively low efficiency of thermoelectric energy conversions. In some instances this low efficiency can be ignored if the cost of the fuel is relatively low. This is particularly true where use is made of the thermal gradients in oceans, geothermal wells and industrial waste streams. However, even with this substantially free energy, for the thermoelectric generator to be competitive it must have an output of electrical power that is less expensive than conventional alternatives. Therefore, to be able to be competitive, it is necessary that the cost of building thermoelectric generators be kept to a minimum.

One of the known types of thermoelectric generators comprises thin thermoelectric semiconductor elements, generally less than one millimeter in thickness, covering only a fraction, generally less than one-third, of the surface area of the heat exchanger. The bismuth telluride-antimony selenide compound is well suited for use in such thermoelectric generators, particularly for the low temperature range, such as about 0°C to about 200°C. In this type of thermoelectric generator, semiconductor elements are arranged in arrays with equal numbers of n-type and p-type semiconductor elements which are electrically interconnected in a series/parallel pattern chosen to provide a desirable voltage and current. In a modification of the above thermoelectric generator, only one type (either n-type or p-type) is used in each array but in the generator module the stacked arrays are alternately n-type and p-type.

3. SUMMARY OF THE INVENTION

It is an object of this invention to provide a method for the continuous production of a substrate comprising a material having good electrical insulating and thermal conducting properties positioned between two layers of metal and wherein means are incorporated to ensure a uniform spacing between the layers of metal.

It is another object of this invention to provide a method wherein thin thermoelectric semiconductor elements are positioned at predetermined locations on substrates and secured thereto in an automated production system.

It is a further object of this invention to provide a method wherein thin thermoelectric semiconductor elements comprising a plurality of laminated layers are positioned at predetermined locations on substrates and secured thereto in an automated production system.

It is another object of this invention to form a thermoelectric generator from substrates having thin thermoelectric semiconductor elements thereon and super-strates.

It is another object of this invention to form a thermoelectric generator having stacked arrays using only one type of semiconductor elements, i.e. n-type or p-type.

Additional objects, advantages and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

This invention relates to a method for fabricating substrates and superstrates for use in thermoelectric generators; for the fabrication of thin thermoelectric semiconductor elements on such substrates; for combining a plurality of substrates having a plurality of thin thermoelectric semiconductor elements thereon and superstrates into a thermoelectric generator; and for forming a thermoelectric generator having only one type of semiconductor elements, i.e. n-type or p-type.

The substrates are formed in a continuous laminating process wherein a thin layer of a low temperature vitreous enamel is fused between two layers of metal foil.

The enamel preferably contains spacing materials, such as small beads of uniform diameter, which remain solid in a liquid molten enamel. The small beads function to insure a uniform spacing between the layers of metal foil. In the preferred embodiment, the metal foil comprises copper but it is understood that other metals having similar properties may be used. Also, the enamel preferably is a lead oxide based vitreous enamel and the small beads are glass beads with a high silica content, although other materials having similar properties may be used.

The substrates are then provided with thin thermoelectric semiconductor elements. Specifically, the substrates move over a series of rollers through a plurality of work stations maintained at pressures comprising only a small fraction of one atmosphere and exit from the final work station with the thin thermoelectric semiconductor elements secured in a predetermined location on the substrates.

A plurality of substrates, each having thin thermoelectric semiconductor elements thereon, are provided with superstrates to form thermoelectric modules. A structure comprising a plurality of spaced apart hollow panels are used with the thermoelectric modules to form a thermoelectric generator. The modules are placed between and in contact with adjacent hollow panels. Appropriate means are provided to flow relatively hot fluids through every other panel and cold fluids through the remaining panels. In the preferred embodiment of the invention only one type of semiconductor element; n-type or p-type is used. Suitable electrical connections are provided so that the electric energy generated by the thermoelectric generator can be used.

The accompanying drawings, which are incorporated in and form a part of the specification illustrate preferred embodiment(s) of the present invention, and together with the description, serve to explain the principles of the invention.

4. BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic illustration of a method for fabricating substrates;

Fig. 2 is a schematic illustration of a portion of a substrate;

Fig. 3 is a schematic illustration of a method for providing substrates with thin thermoelectric semiconductor elements;

Fig. 4 is a schematic illustration of a method for depositing various materials on a substrate;

Fig. 5 is a pictorial representation of the lamination of a substrate having thin thermoelectric semiconductor elements secured thereon with a superstrate;

Fig. 6 is a schematic illustration of a thermoelectric generator; and

Fig. 7 is a schematic illustration of an electric circuit for use with the thermoelectric generator of Fig. 6.

5. DETAILED DESCRIPTION OF THE INVENTION

In Fig. 1, there is illustrated a method for fabricating substrates for use in thermoelectric generators. A coil 2 of a metal foil 4 is rotatably mounted at one end 6 of a continuous conveyor 8 so that the metal foil 4 may be removed from the coil 2 and deposited on the conveyor 8. A hopper 10 is located above the conveyor 8 and contains a continuous supply of material 12 to be deposited through an opening 14 onto the upper surface of the metal foil 4. The material 12 may comprise any material having good electrical insulating properties and good thermal conducting properties and in the preferred embodiment comprises a mixture of vitreous enamel and a plurality of small beads for a purpose to be described below. The conveyor 8 is maintained in continuous motion by suitable means (not shown).

After being deposited on the metal foil 4, the material 12 passes under a series of heaters 16 which apply sufficient heat to the material 12 so as to liquefy the vitreous enamel. Another coil 18 of a metal foil 20 is rotatably mounted above the conveyor 8 so that the metal foil 20 may be removed from the coil 18 and deposited on the liquefied material 12. A second conveyor 22 is located above a portion of the conveyor 8 and is maintained in continuous motion by suitable means (not shown). The laminate, comprising the metal foil 4, the liquefied material 12 containing the small beads and the metal foil 20, moves into position between the conveyors 8 and 22. The conveyor 22 exerts a predetermined pressure on the metal foil 20 so as to force the foil 20 against the liquefied material 12. Movement of the foil 20 against the liquefied material 12 is limited by the small beads. The space between the metal foil 20 and the metal foil 4 is kept uniform by the small beads being in contact with the metal foil 4 and the metal foil 20. During the passage between the conveyors 8 and 22, the liquefied vitreous enamel hardens and is fused to the adjacent surfaces of the layers of metal foils 4 and 20. At the ends 24 and 26 of the conveyors 8 and 22, suitable means 28 and 30 are provided to cut the continuous laminate of the metal foil 4, the vitreous enamel and small beads and the metal foil 20 into predetermined lengths so as to form substrates 32. A conveyor 34 is provided for moving the substrates 32 to another location for further processing.

In Fig. 2, there is illustrated a portion of a substrate 32 comprising the metal foil 4, the vitreous enamel 36, the small beads 38 and the metal foil 20. In the preferred embodiment, the metal foil comprises copper having a thickness of from about 0.0012 to about 0.003 of an inch. The vitreous enamel 36 comprises a lead oxide based vitreous enamel. The small beads 38 comprise glass having a high silica content and have an average diameter of about 0.002 inch. The heaters 16 supply sufficient heat to raise the temperature of the material 12 to about 600°C so as to liquefy the lead based vitreous enamel 36.

A system for processing substrates 32 so as to provide them with thin thermoelectric semiconductor elements is schematically illustrated in Fig. 3. A conveyor 40 transports a plurality of support plates 42 through a series of work stations. The support plates 42 are spaced a predetermined distance from each other and are moved through the work stations by a plurality of power driven transport rollers 44. In most instances, the support plate 42 and the substrates 32 are of generally the same size. However, it is to be understood that the support plates 42 can be substantially larger than the substrates 32 so that a plurality of substrates can be positioned on each support plate. A substrate 32 is positioned in a predetermined location on each of the support plates 42 so that the thin thermoelectric semiconductor elements will be properly positioned. The movement of the power driven transport rollers is controlled by signals generated by a computer (not shown) to move the support plates 42 over the conveyor 40 and to locate each support plate at a predetermined location at each work station.

After being deposited on a support plate 42, a substrate 32 is moved through an air lock chamber 46 and then into a buffer chamber 48 wherein the pressure is reduced to a small fraction of an atmosphere, such as from about 100Pa to about 1000Pa. The substrate then passes through another air lock chamber 50 into a cleaning chamber 52 wherein the substrate 32 is exposed to a cleaning operation, such as a plasma of ionized gas, so as to prepare the substrate for the deposition thereon of a thin thermoelectric semiconductor element. The substrate 32 then passes through one or more air lock chambers 54 and 56 into another buffer chamber 58 wherein the pressure is further reduced to from about 10^{-1}Pa to about 10^{-2}Pa.

The cleaned substrate 32 leaves buffer chamber 58 and passes through a plurality of material deposition chambers 60, 62, 64 and 66. The material deposition chambers 60, 62, 64 and 66 are maintained at pressures of from about 10^{-1} ~~10^{-2}~~ Pa to about 10 ~~10^{-3}~~ Pa during deposition. As illustrated in Fig. 3, the dimensions of each chamber 60, 62, 64 and 66 correspond generally to the dimensions of each support plate 42 so that the substrate 32 may be readily positioned in the proper predetermined location in each of the chambers 60, 62, 64 and 66. In each of these material deposition chambers, one of the materials to be laminated together to form the thermoelectric semiconductor elements is deposited at predetermined spaced locations on the substrate 32 by a sputtering process schematically illustrated in Fig. 4. A magnet 68 is mounted in a fixed position in each of the material deposition chambers spaced a predetermined distance above the substrate 32 on the support plate 42. A sputtering target 70 is positioned below the magnet 68 and comprises a supply of the material to be deposited on the substrate 32. Immediately below the sputtering target 70, there is an anode 72 having an inner configuration greater than the sputtering target 70. The sputtered atoms 74 move downwardly through a mask 75 having suitable openings therein to be deposited on the substrate 32.

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In some instances, the mask 75 may be omitted and a continuous layer of material may be deposited on each substrate. However, since economic considerations are important, the mask is used in most instances. That is, because the difference between thermoelectric generation of electric energy by a continuous layer and thermoelectric generation by spaced locations of the thin thermoelectric semiconductor elements is relatively small, the mask is typically used.

In the preferred embodiment of the invention, the sputtering targets 70 are as follows: nickel in deposition chamber 60; bismuth telluride-antimony selenide in deposition chamber 62; nickel in deposition chamber 64; and solder in deposition chamber 66. The thin thermoelectric elements 76 are illustrated in Fig. 5 wherein each element comprises a layer 78 of nickel secured to the substrate 32; a layer 80 of bismuth telluride-antimony selenide secured to the layer 78 of nickel; a layer 82 of nickel secured to the layer 80 of bismuth telluride-antimony selenide; and a layer 84 of solder secured to the layer 82 of nickel. The layers 78 and 82 of nickel function as diffusion barrier layers and the layer 80 of bismuth telluride-antimony selenide is the thermoelectric semiconductor film. The substrate 32 moves from deposition chamber 66 through a plurality of buffer chambers 88 and air locks 86 wherein the pressure is gradually increased to substantially one atmosphere.

In Fig. 5 there is illustrated a superstrate 90 about to be positioned in contact with the layers 84 of solder. The superstrate 90 is similar to the substrate 32 and comprises metal foil 4, vitreous enamel 36, small glass beads 38 and metal foil 20. After the superstrate 90 has been moved into contact with the layers 84 of solder, a low temperature soldering or brazing operation is used to secure the metal foil 4 to the layers 82 of nickel.

A thermoelectric generator is illustrated schematically in Fig. 6 and uses a plurality of thermoelectric modules 92 wherein each thermoelectric module 92 comprises a substrate 32 and a superstrate 90 having thin thermoelectric semiconductor elements 76 therebetween. A structure comprising spaced apart hollow panels 94, 96, 98 and 100 is provided so that the plurality of thermoelectric modules 92 may be positioned between and in contact with the hollow panels 94, 96, 98 and 100. As shown in Fig. 6, one side of each thermoelectric module 92 is adjacent to a cold fluid and the other side is adjacent to a hot fluid. The panels 94 and 98 are connected to means 101 through which cold fluid is supplied and to means 102 through which the cold fluid is removed. The panels 96 and 100 are connected to means 104 through which hot fluid is supplied and to means 106 through which the hot fluid is removed. The number of panels 94, 96, 98 and 100 used will depend on the size of thermoelectric generator desired. In the thermoelectric generator illustrated in Fig. 6, only one type of semiconductor element, i.e. n-type or p-type, is used. The use of only one type of semiconductor element is advantageous since at various times the costs of the materials is different so that the most economical material may be selected. Also, since only one type is being used, the manufacturing process does not have to be interrupted.

In some instances, the metal foil 20 may be omitted so that in the assembled thermoelectric generator there will be no metal layer between the material 12 having good electrical insulating properties and good thermal conducting properties and the surfaces of the panels 94, 96, 98 and 100. For manufacturing purposes, the upper conveyor 22 would comprise a material which would not stick to the material 12.

In Fig. 7, there is illustrated an electrical circuit for use with a thermoelectric generator as illustrated in Fig. 6 and wherein the semiconductor element is n-type. The negative and positive sides of the thermoelectric modules 92 are connected in series.

The foregoing is considered as illustrative only of the principles of the invention. Further, since numerous modifications and changes will readily occur to those skilled in the art, it is not desired to limit the invention to the exact construction and operation shown and described, and accordingly all suitable modifications and equivalence may be resorted to falling within the scope of the invention as defined by the claims which follow.

ABSTRACT

A thermoelectric generator using semiconductor elements for responding to a temperature gradient to produce electrical energy with all of the semiconductor elements being of the same type is disclosed. A continuous process for forming substrates on which the semiconductor elements and superstrates are deposited and a process for forming the semiconductor elements on the substrates are also disclosed. The substrates with the semiconductor elements thereon are combined with superstrates to form modules for use thermoelectric generators.

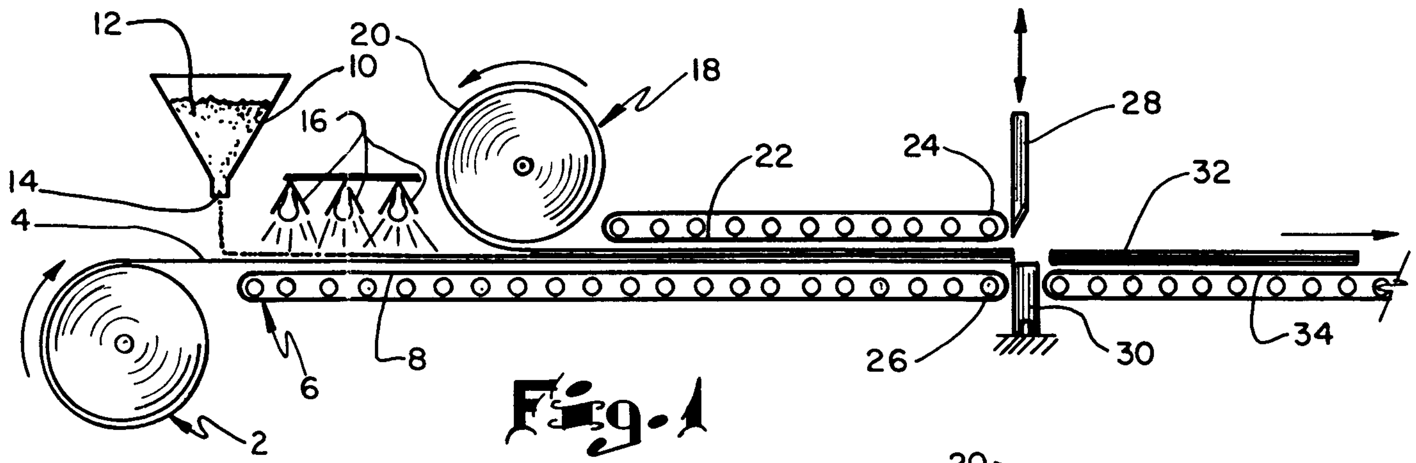

Fig. 1

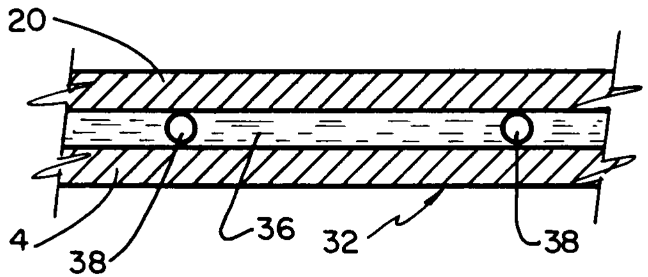

Fig. 2

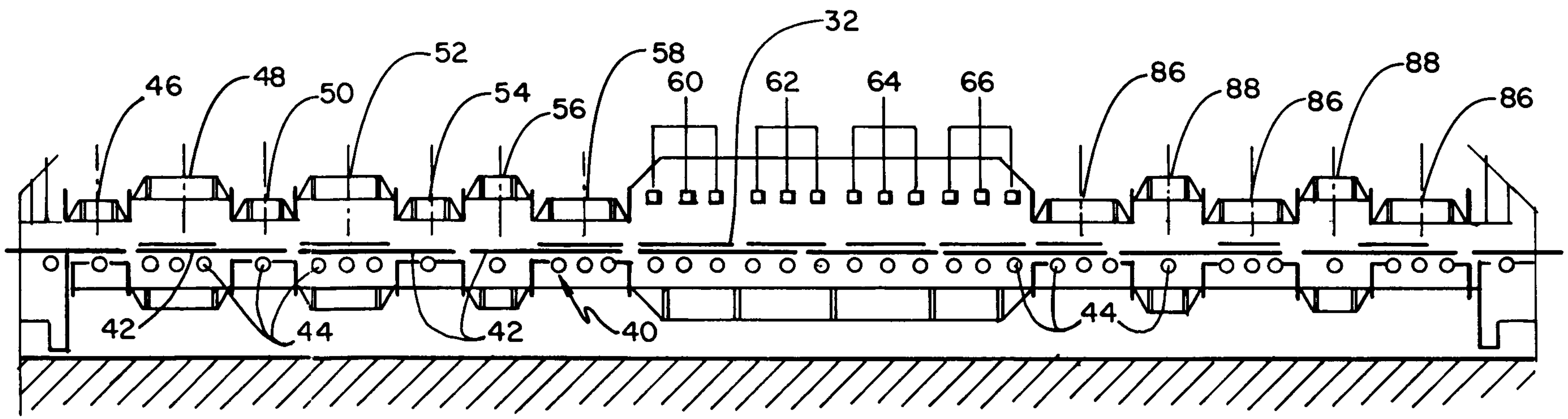

Fig. 3

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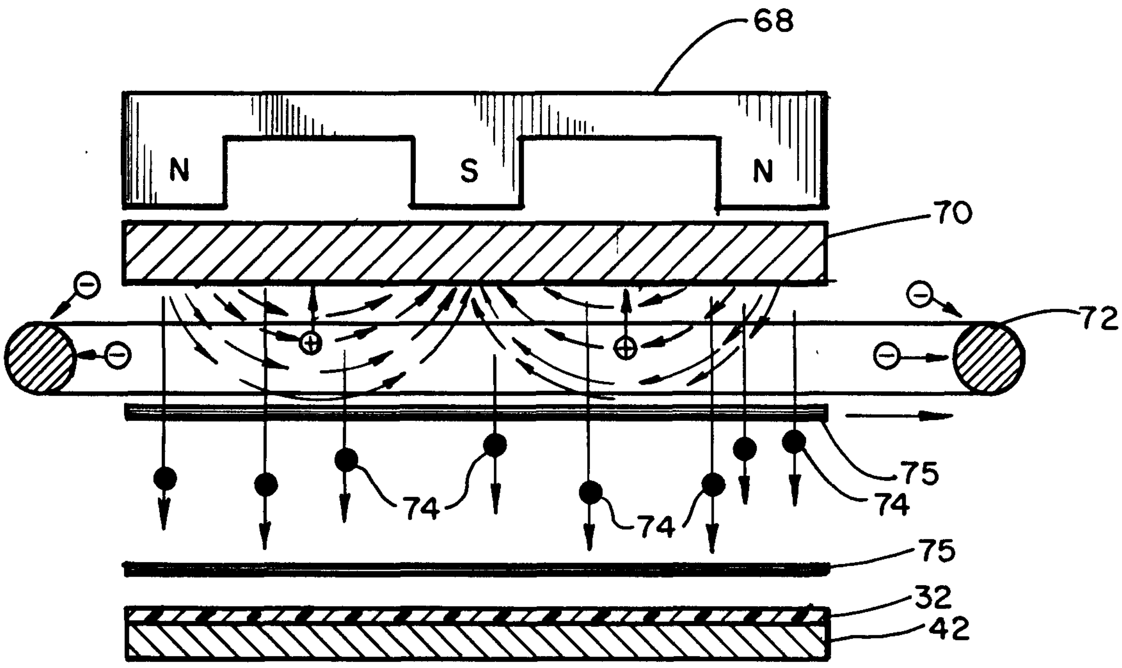
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Fig. 4

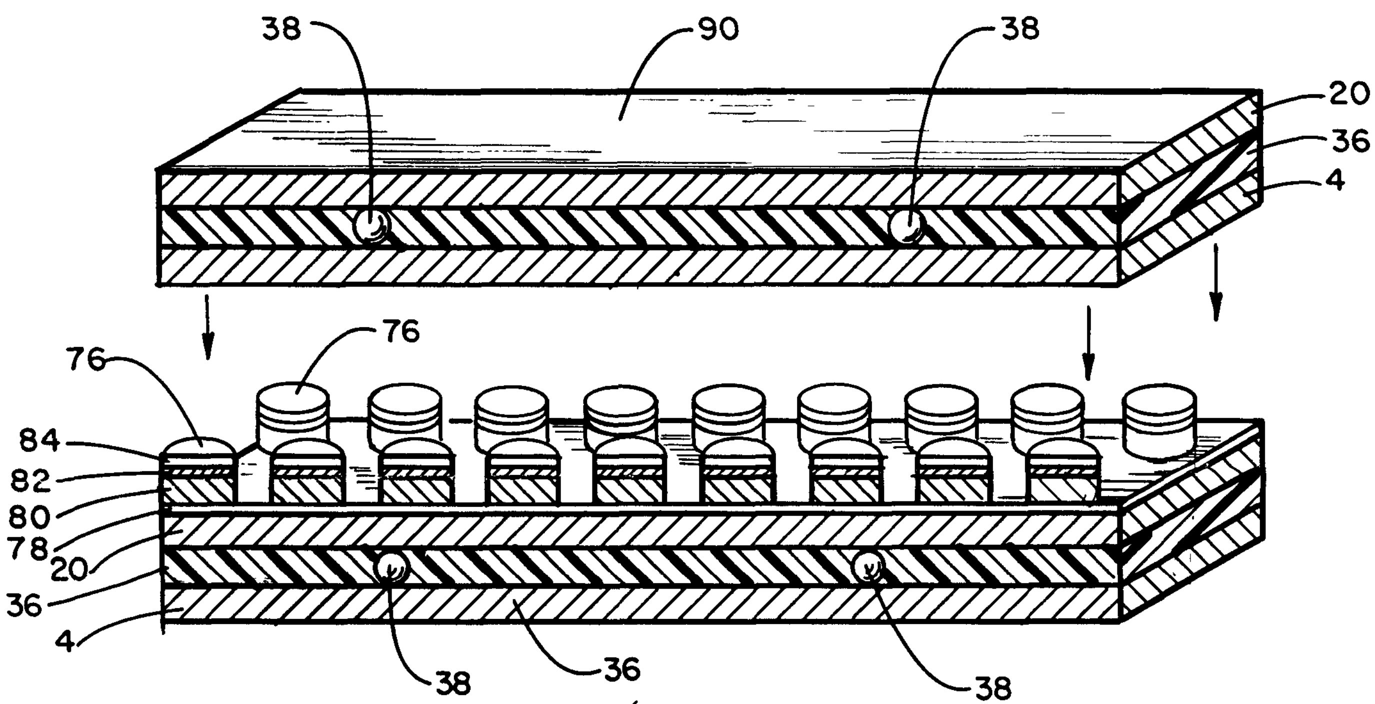
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Fig. 5

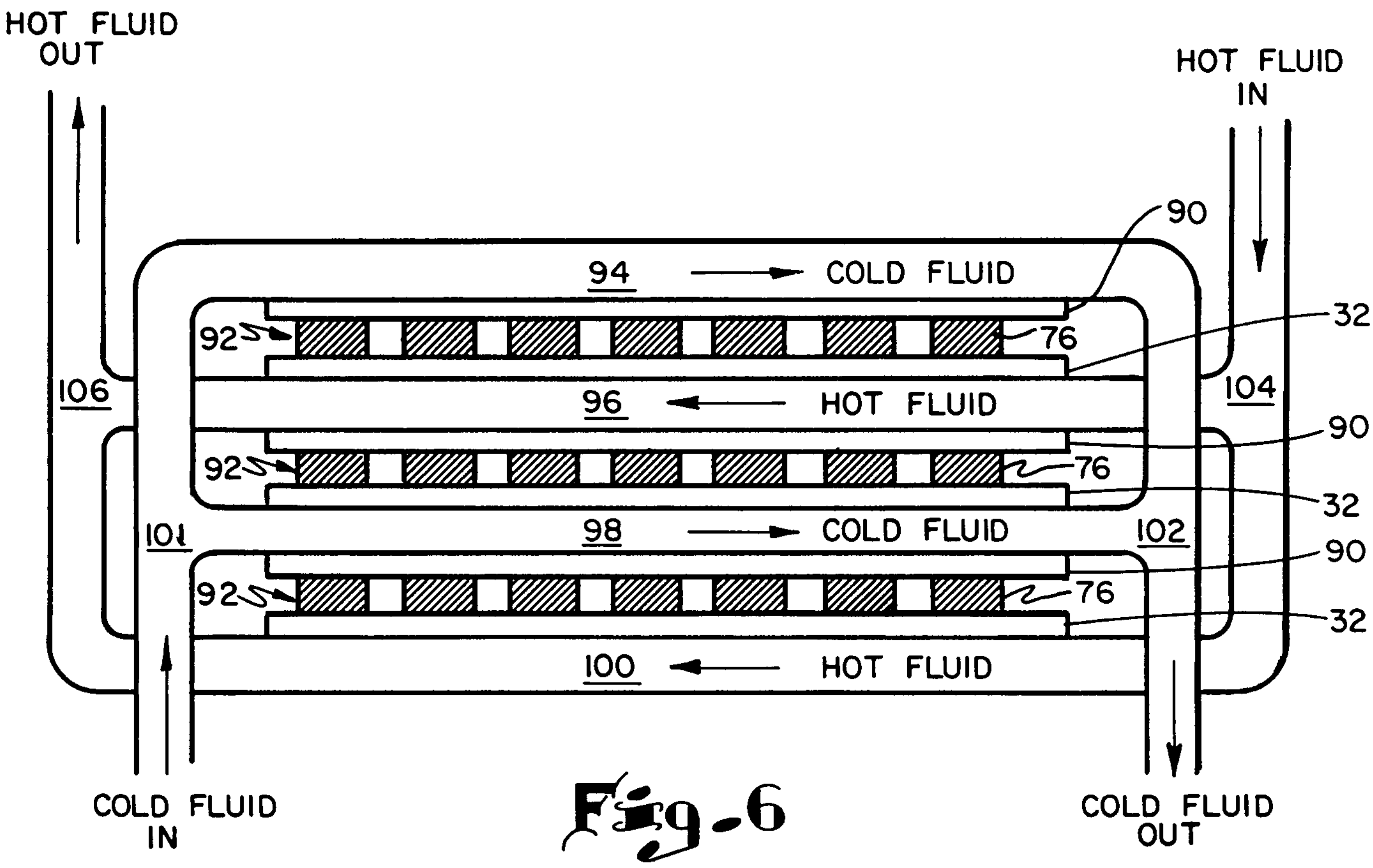
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Fig. 6

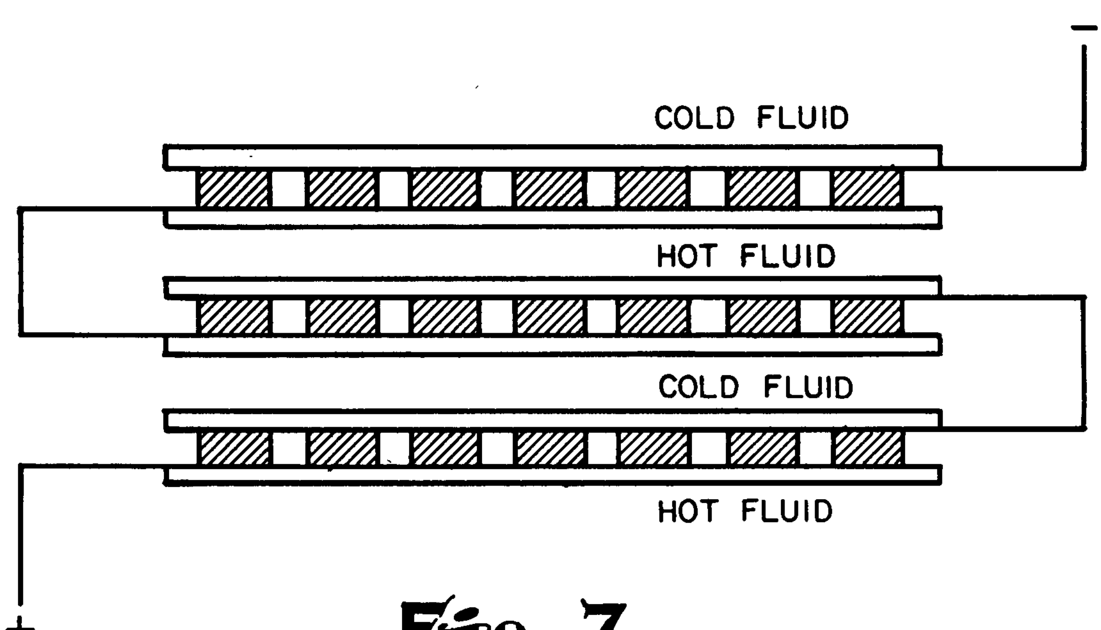
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Fig. 7