United States Patent

[11] **3,601,887**

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[73] Assignee **Westinghouse Electric Corporation**
Pittsburgh, Pa.
Continuation-in-part of application Ser. No. 593,528, Nov. 10, 1966, now abandoned.

[54] **FABRICATION OF THERMOELECTRIC ELEMENTS**
13 Claims, 6 Drawing Figs.

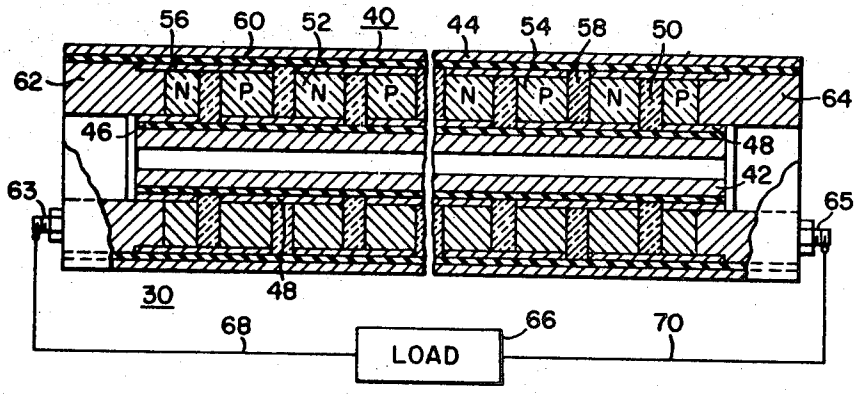
[52] **U.S. Cl.** **29/573,** 136/201, 136/202
[51] **Int. Cl.** **B01j 17/00,** H011 15/00, H01n 49/00
[50] **Field of Search** 29/573; 72/367; 136/201, 202

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ABSTRACT: An isostatic hot compressing process step is employed to exert a pressure of from 5,000 p.s.i. to 50,000 p.s.i. on the exterior surfaces only of a hollow cylindrical thermoelectric element having thermoelectric material disposed between exterior and interior cylindrical shell members to plastically deform the exterior surfaces of the element and reducing the annular cross-sectional area of the element from 1 percent to 15 percent to provide at least an intimate physical contact between the body of thermoelectric material contained therein and the inner and outer members of the element. The inner member of the element is in compression after the hot isostatic compression is removed. Isostatic cold compressing may be applied to the element prior to the isostatic hot compressing process step.



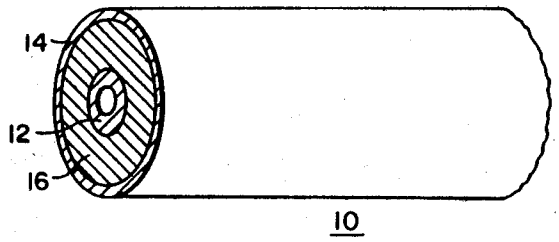


FIG. 1.

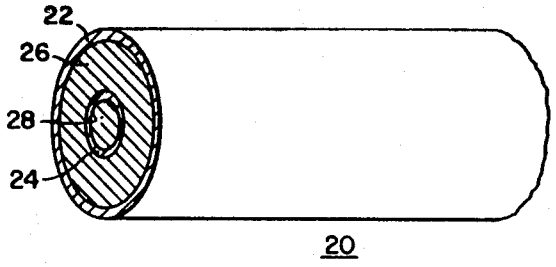


FIG. 2.

FIG. 3.

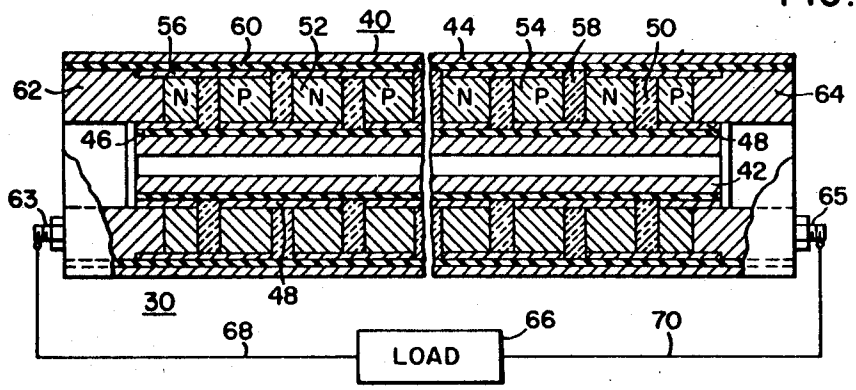


FIG. 4.

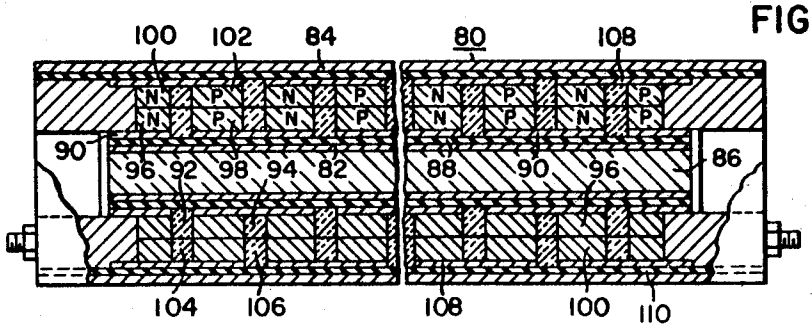


FIG.5.

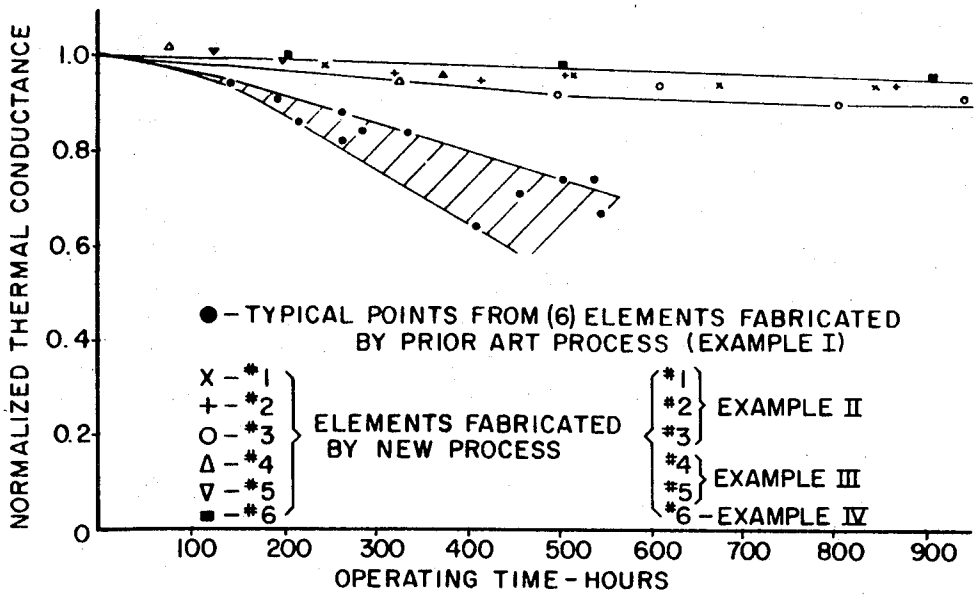
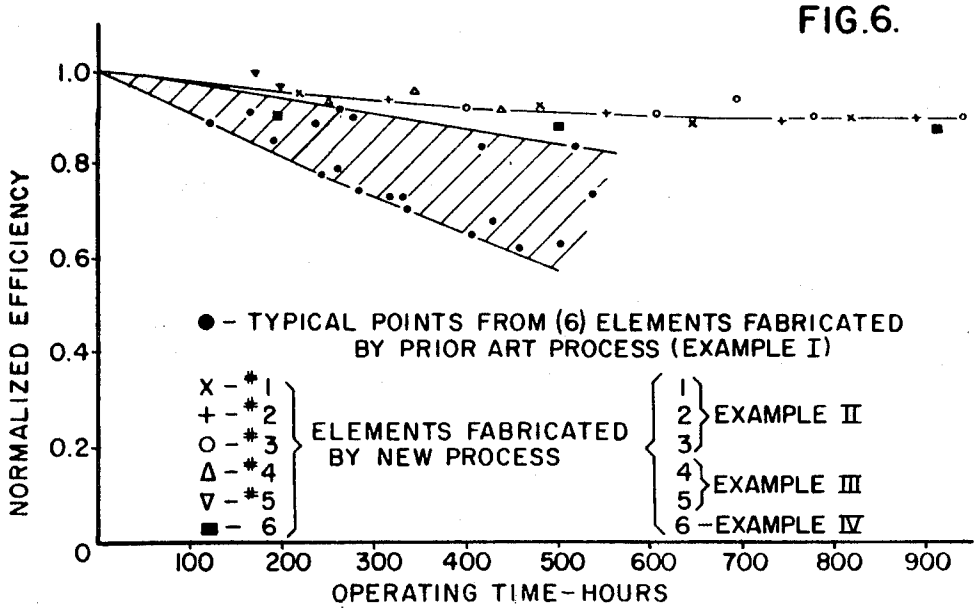

NORMALIZED THERMAL CONDUCTANCE
1.0
0.8
0.6
0.4
0.2
0
100
200
300
400
500
600
700
800
900
OPERATING TIME - HOURS
● - TYPICAL POINTS FROM (6) ELEMENTS FABRICATED BY PRIOR ART PROCESS (EXAMPLE I)
X - #1
+ - #2
O - #3
Δ - #4
∇ - #5
■ - #6
ELEMENTS FABRICATED BY NEW PROCESS
#1
#2
#3
EXAMPLE II
#4
#5
EXAMPLE III
#6 - EXAMPLE IV

FIG.6.


NORMALIZED EFFICIENCY
1.0
0.8
0.6
0.4
0.2
0
100
200
300
400
500
600
700
800
900
OPERATING TIME - HOURS
● - TYPICAL POINTS FROM (6) ELEMENTS FABRICATED BY PRIOR ART PROCESS (EXAMPLE I)
X - #1
+ - #2
O - #3
Δ - #4
∇ - #5
■ - 6
ELEMENTS FABRICATED BY NEW PROCESS
1
2
3
EXAMPLE II
4
5
EXAMPLE III
6 - EXAMPLE IV

FABRICATION OF THERMOELECTRIC ELEMENTS

This application is a continuation-in-part of our application Ser. No. 593,528, filed Nov. 10, 1966, now abandoned, the assignee of which is the same as that of the present application.

The present invention relates to a process for preparing thermoelectric elements.

A prior process employed to fabricate hollow cylindrical thermoelectric elements which comprise an outer cylinder member and a smaller inner cylindrical member disposed therein with the thermoelectric material proper being placed in the space between them, utilizes apparatus and techniques exerting a high pressure upon both the outer surface of the outer cylindrical member and the inner surface of the inner cylindrical member of the elements. The application of the pressure at a high temperature upon both outer and inner cylindrical surfaces reduces the diameter of the outer cylindrical member and increases the diameter of the inner cylindrical member. It should be noted that the inner cylindrical member is stretched or elongated in the process. This process eliminates radial assembly gaps between the components of the element, densifies the thermoelectric material and establishes a good thermal contact at each radial interface.

However, when an element processed in this manner is operated at an elevated temperature, the inner cylindrical member has reduced efficiency. This has been found to result from the fact that the innermost member relaxes inwardly, thereby reducing its contact pressure upon the adjoining components of the element. The resulting reduction in contact pressure increases the thermal contact resistances within the element, thereby causing a reduction in the efficiency of the element.

An object of this invention is to provide a process for producing hollow cylindrical thermoelectric elements having the innermost portions in compression whereby the innermost cylindrical portions do not undergo relaxation when the elements are operated at a high temperature.

Another object of this invention is to provide a process for manufacturing a hollow cylindrical thermoelectric element by applying isostatic pressure only to the outer surface whereby the element is collapsed onto a heat source within the hollow member, thereby assuring a good thermal conductivity relationship between the cylindrical element and heat source, thereby preventing inward relaxation of the thin wall member when the element is operated at a high temperature.

A further object of this invention is to provide a process for manufacturing a hollow cylindrical thermoelectric element embodying a thick wall inner cylindrical member to develop a compressive stress on the innermost portions adjacent the thick wall whereby when the element operates at a high temperature the thick wall inner cylindrical member maintains good thermal contact with the adjoining components of the element.

Other objects of this invention will, in part, be obvious and will, in part, appear hereinafter.

For a better understanding of the nature and objects of this invention, reference should be had to the following detailed description and drawings, in which:

FIGS. **1** and **2** are perspective views, partly in cross section, of thermoelectric elements made in accordance with the teachings of this invention;

FIGS. **3** and **4** are views, partly in cross section, of thermoelectric elements made in accordance with the teachings of this invention;

FIG. **5** is a graph comparing the normalized overall efficiency of thermoelectric elements made by a prior art process and compared with thermoelectric elements made in accordance with the teachings of this invention; and

FIG. **6** is a graph comparing the normalized thermal conductance of thermoelectric elements made by a prior art process and compared with thermoelectric elements made in accordance with the teachings of this invention.

In accordance with the present invention and in attainment of the foregoing objects there is provided a process for producing an integral thermoelectric element, the steps comprising disposing a thermoelectric material, or a plurality of layers of thermoelectric material, within a hollow compartment defined by the outer wall of an inner metal member and the inner wall of a larger diameter outer metal member, the metal members being concentric with each other, sealing the ends of the compartment to retain the thermoelectric material therein and to prevent substantial pressure developing in the hollow, preferably evacuating the compartment, and hot pressing the entire assembly at a temperature from about 250° C. to slightly below the melting temperature of the lowest melting temperature component in the assembly by the application of an isostatic pressure of from 5,000 p.s.i. to 50,000 p.s.i. or higher to a selected surface area of only the outer metal member to effect a reduction of from 1 percent to 15 percent in the cross-sectional area of the compartment to provide at least an intimate physical contact, and in some instances a metallurgical bond between the thermoelectric material and the walls of the metal members and increasing the density of the thermoelectric material by 4 percent to 10 percent. The process results in a compressive stress being imparted to the innermost layers after the pressure is released.

In one preferred embodiment of the invention, a plurality of compressed bodies of powdered thermoelectric material are assembled within the space between an inner and outer cylindrical metal member. Electrical insulation is interposed between portions of the bodies. Bridging electrical contacts are disposed between certain portions of the bodies of thermoelectric material with the insulation being disposed between the cylindrical members and the bridging members, to provide a closely packed assembly. The inner cylindrical metal member is hollow and has a thin wall and this hollow is completely filled with a solid heat source such, for example, as a radioisotope, or a nuclear reactor fuel, for example UO_2, and is sealed to prevent fluid pressure developing therein during subsequent processing.

The entire assembly is hot pressed at an isostatic pressure of from about 5,000 p.s.i. to 50,000 p.s.i. at a temperature of from about 250 degree C. to the melting temperature of the lowest melting temperature component of the assembly until the space between the inner and outer cylindrical members has a reduction in cross-sectional area of from about 1 percent to 15 percent to provide a metallurgical bond between the thermoelectric bodies, the metal members and the bridging electrical contacts and to increase the density of the thermoelectric material by about 1 percent to 10 percent. The thin wall of the inner cylindrical member will be collapsed upon the surface of the solid heat source so that the two are in an intimate physical contact and a good thermal conductivity relationship with each other.

In an alternate and preferred embodiment of the invention, the components are the same as in the first preferred embodiment except that the inner cylindrical member is a thick walled hollow tube. Prior to processing, the bore of the thick wall hollow tube is hermetically sealed to exclude autoclave gas. One method of hermetically sealing the tube is to fill the tube with a closely fitting solid metal bar which is then seal welded to the ends of the inner tube. Another suitable method of hermetically sealing the bore of the tube is to insert an end plug into each end of the tube and seal each plug therein. The tube bore may be evacuated, filled with air, or filled with an inert gas. Additionally, various solid fillers such, for example, as solid cylindrical punchings of metal, metal bars or metal rods may be stacked or otherwise disposed within the bore of the tube prior to inserting the end plugs and welding them to the tube. The solid filler must physically support the inner wall of the tube bore and be nonreactive with the material of the cylindrical member during processing of the device.

In each instance of the alternate and preferred embodiment of this invention, the assembled components are hot pressed by applying an isostatic pressure to the exterior surface of the

assembled components only thereby reducing the diameter of each cylindrical component layer, and radially compressing the inner cylindrical member rather than stretching it as in prior art devices.

The thermoelectric materials employed herein may comprise metallic and nonmetallic substances such, for example, as solid or powdered metals, ceramics or semiconductors or mixtures of two or more. The thermoelectric members may be preliminarily prepared by compressing powdered thermoelectric materials in a suitable die to a density of about 85 percent and higher, or by casting in a manner known to those skilled in the art. The insulating materials employed as partition members and the like between thermoelectric bodies may comprise any good inorganic electrical insulators such, for example, as silica, mica, alumina, boron nitride, beryllium oxide and inorganic silicates such as boron silicate and lime glasses and those materials comprising the reaction product of mica lead borate glass sold under the trade name of Mycalex and materials comprising magnesium silicates sold under the trade name Lavite. The cylindrical metal members may comprise a good electrically and thermally conductive material, such as silver, aluminum, nickel, stainless steel, pure iron and copper or base alloys thereof.

In the preferred embodiments of the invention, there is provided an integral, elongated, thermoelectric element comprising a series of washer-shaped P- and N-type thermoelectric bodies electrically joined in series within a compartment provided between an outer cylindrical metal member and an inner cylindrical metal member electrically insulated therefrom but in good thermal conducting relation therewith. The thermoelectric element includes a plurality of inner and outer bridging metal ring members on an insulated cylindrical metal member disposed between successive thermoelectric washers. The bridging ring members may be electrically insulated from the cylindrical members by disposing a relatively thin insulating member therebetween either prepared separately as when employing a material such a boron nitride or mica, or produced in situ by plasma jet spraying an insulating material, such as alumina, on the walls of the cylindrical members. When employing a series of adjacent bridging ring members, they will be electrically insulated from each other. The bridging ring members may comprise any good electrically conductive metal such, for example, as nickel, copper, aluminum, iron or base alloys thereof.

A plurality of compressed washers of powdered thermoelectric material are disposed with one inner diameter face on the inner bridging ring members and an outer bridging metal ring member disposed on the outer periphery of the compressed washer of thermoelectric material so that the thermoelectric washer members are electrically connected at each peripheral face or diameter thereof by either the inner or outer concentric bridging ring members while successive washers are electrically insulated from each other at the other diameter or peripheral face. The insulating materials employed between the thermoelectric washers may comprise any of the electrical insulators described previously with respect to the partition members of the less complicated configurations.

The number of thermoelectric washer members employed will determine the number of metal bridging ring members needed to provide electrical contact therebetween. It is preferred that each pair of thermoelectric washers electrically contacting each other consist of a P-type thermoelectric material and an N-type thermoelectric material. The components of the assembly are as closely packed as is possible so that the total free or gap space in the assembly is not above about 1 percent of the diameter of the outer cylindrical member.

The resulting elongated thermoelectric member after being fully processed by isostatic compressing has electrical leads attached to the end thermoelectric washers so that they may be connected in an electrical circuit.

In certain embodiments of the invention a complete thermoelectric device is not produced in a single operation. Thus, a single P or N-type thermoelectric body is bonded metallurgically to the walls of two concentrically disposed cylindrical metal members. In this case the resulting isostatically processed member having its inner walls under compressive stress may be severed into a plurality of cylindrical units of any desired length which may be further machined to shape or size, or the member may be severed into relatively small individual thermoelectric pellets of desired shape. The cylindrical units or pellets may be joined to other thermoelectric pellets of opposite type to produce a stack of composite thermoelectric elements and assemblies which may be electrically connected, and suitably insulated both electrically and thermally, into thermoelectric power generators or cooling devices.

It is particularly desirable in all embodiments of the invention that the interior of the unit being deformed or hot pressed be evacuated prior to deformation to remove all reactive gases.

The terms "isostatic pressure," "isostatic deformation," "isostatic cold pressing" or "isostatic hot pressing" as used herein refer to a method involving the application of high enough pressures for reducing the cross-sectional area of a member to a sufficient degree to plastically deform and urge adjacent components into an intimate physical contact with each other, and even bond a component to the mating face of another adjacent contacting component, the pressures being uniformly applied or induced to all the exterior surfaces by using gases and/or liquids as a compressing medium. Although the preferred pressure range is from 5,000 to 50,000 p.s.i., it should be appreciated that higher and, in some instances, slightly lower pressures may be employed depending upon the materials involved in the assembly, the temperature, time of application of temperature and pressure, and other factors. It should be understood also, that an intimate physical contact, and when required, good metallurgical bonds between mating faces should be obtained, and when initial close tolerances between components are present, the amount of deformation required to provide the intimate physical contact and good bonds may be 1 percent or even less.

The temperatures employed in the process are selected by reference to the materials and their properties. In assemblies where some of the components may have large differences in thermal expansivity, in order to minimize joint stresses on cooling the joining temperatures should be selected at the lowest possible temperature which will effect a satisfactory bond of all component. Generally, the temperature chosen by the above consideration will be best for bonding any assembly whether there is expansivity mismatch between components or not. Other considerations are modulus of elasticity of the various materials and quality of the bonds in order to achieve the best bonded assembly with the minimum of internal stresses.

The period of time of application of temperature and pressure is selected by the consideration of allowing all parts of the assembly to achieve thermal equilibrium, and that of allowing solid-state diffusion to occur to effect the metallurgical bonds between adjacent contacting components of the assembly. If necessary, this latter requirement is readily determined by experiment in each case. Experimental data has indicated that many metallurgical bonds can be formed in as little as 15 minutes of heating, but periods of 2 hours appear to be more reliable. Bonding may be speeded up, or accomplished at lower temperatures or pressure, if desired, by adding joint bond promoters of various kinds, such as rapidly diffusing elements as is well known in the art.

By the isostatic process disclosed herein, all the bonds between all the components of the thermoelectric element may be formed in a single operation. That is, the complete assemblies are disposed in a suitable pressure vessel, such as an autoclave containing a heating coil and the desired temperatures, pressures and times for the particular assembly are imposed. After removal from the pressure vessel all the necessary bonds have been provided so that the only processing

necessary thereafter is of a mechanical nature, such as cleaning and applying leads, so that the completed unit may be integrated in some type of an electrical circuit.

Referring to FIG. 1, there is shown an isostatically hot pressed thermoelectric element **10**, after one end of the element is removed as by machining, consisting of an inner thick wall hollow cylindrical metal contact member **12** and an outer cylindrical concentric metal contact member **14** with a body **16** of compressed powdered thermoelectric material disposed therebetween and metallurgically bonded to the walls of the metal members **12** and **14**. Surprisingly, good bonding is effected between the metal walls **12** and **14** with the body **16**. The thermoelectric material body **16** may consist of any one of the P or N-type thermoelectric materials or two or more suitable layers in any desired arrangement or sequence.

The metals used in forming the members **12** and **14** are selected on the basis of their compatibility with the thermoelectric material, desired electrical and thermal characteristics and resistance to the corrosive atmospheres for a given application.

The wall thickness of tubular member **12** is sufficient so that the tube will not collapse when subjected to the autoclave temperature and pressure. The entire assembly is evacuated, the material **14** sealed off with a cap and the ends of member **12** are capped to prevent any appreciable pressure developing therein. When subject to the pressure of the autoclave of up to 50,000 p.s.i. or more at the desired temperature, the inner tube **12**, as well as the adjacent layers of material **14**, are compressed rather than stretched as in prior art devices. In subsequent service upon being heated to a high temperature, the member **12** expands partly due to the retained compressive stress, whereas prior art devices contracted. The ability of the member **12** to expand at the high temperature enables it to remain in a good thermal conductivity relationship with the thermoelectric component **16** of the element **10** thereby preventing degradation of efficiency of element **10** due to loss of contact pressure between adjacent components.

When employing the isostatically hot pressed thermoelectric element **10** or a section thereof in an operational device, it is often desirable to connect two or more of either P or N-type or alternate P-N-type elements in a particular type of arrangement and circuitry.

If it comprises the hot junction of a refrigerating device, the inner hollow contact member **12** not only serves to carry electrical current, but enables a cooling fluid such as water or air to be conveyed to dissipate heat. If the element **10** is employed as part of an electrical generator, hot gases, liquid or other heat source may be disposed in or passed through the hollow contact member **12**. The outer contact member **14** may cool a space or it may dissipate heat to a cold sink in either of these cases. The functions of the outer contact member **14** and the inner contact member **12** can be reversed.

With reference to FIG. 2 there is shown a thermoelectric element **20** which is another desirable embodiment of this invention.

The element **20** comprises two concentric cylindrical metal members, an outer member **22** and an inner member **24**. A body **26** of thermoelectric material is disposed in the compartment defined by the outer wall of the inner member **24** and the inner wall of the outer member **22**. A solid heat source **28** such, for example, as a radioisotope or a nuclear reactor fuel such as UO_2 disposed in a refractory, is disposed within and closely fills the hollow inner member **24**. The assembly is evacuated and plugs seal up and ends **22** and **24** so that no hydrostatic pressure enters interiorly.

The inner member **24** has a thin wall capable of being collapsed upon the solid heat source when subjected to the temperature and pressure of the autoclave during the isostatic compression of the element **20**. Further, the wall **24** is put into compression by the pressure transmitted from wall **22** through the consolidation of material **26**. A dense unitary element **20** is produced wherein the heat source **28** is in intimate contact with walls of member **28** and it in turn is in good intimate contact with material **26** and so on. The heat source **28** is also in compression after the isostatic compression process step so that good heat flow occurs.

Referring to FIG. 3, there is shown a thermoelectric device **30** comprising an isostatically deformed complete thermoelectric element **40** embodying the teachings of this invention. The element **40** comprises a thick wall inner cylindrical metal member **42** and a concentric outer cylindrical metal member **44**.

An insulating hollow cylindrical layer **46** is disposed about and joined to member **42**. The layer **46** comprises a material such, for example, as alumina, porcelain, mica and boron nitride. However, the insulating material may be plasma jet sprayed on the outer surfaces of the inner cylindrical member **42**.

A plurality of inner bridging ring members **48** are disposed about and joined to the insulating layer **46**. The ring members **48** are electrically insulated from each other by means of insulating washers **50** comprising materials, such as mica, or those selling under the trade name of Lavite or Mycalex (the latter being a glass-mica reaction product).

A plurality of N-type thermoelectric material washer members **52** and a plurality of P-type thermoelectric material, preferably previously preformed under pressure, washer members **54** are alternately disposed on and joined to the bridging metal ring members **48**.

A plurality of outer bridging metal ring members **56** are disposed on, and joined to, the thermoelectric washer members **52** and **54**, the ring members **56** each contacting a pair of adjacent P and N-type thermoelectric washer members **52** and **54**. The ring members **56** are electrically insulated from each other by means of insulating washers **58**. The insulating washers **58** may comprise the same material as the insulating washer **50**. The washers **58** have a larger outside diameter and a larger inside diameter than the corresponding diameters of washers **50**.

A hollow concentric insulating cylindrical layer **60** comprising a material such as that employed for layer **46**, is disposed about, and joined to, the outer ring members **56**. The outer cylindrical metal member **44** is disposed about and joined to the insulating cylindrical layer **60**.

The components of element **30**, such as the thermoelectric washer members **52** and **54**, bridging members **48** and **56**, and the insulating washers **50** and **58** are slipped into the space between cylindrical members **40** and **42** with their applied insulating layers **46** and **60** already applied. The smallest possible clearance is provided. The ends of the assembly are capped by welding a disk at each end and the interior is evacuated through a hole or tube left in place, which opening is then sealed off. The assembly is then heated and compressed in an autoclave at pressures of up to 50,000 p.s.i. to consolidate the whole into a bonded element.

The isostatic hot pressing operation provides an intimate and effective metallurgical bond between the bridging metal ring members **48** and **56** and the adjoining thermoelectric washers **52** and **54** so as to provide a good electrical contact to each thermoelectric washer member **52** and **54** whereby the thermoelectric washer members **52** and **54** are electrically connected in series. A good thermal conductivity relationship allowing good heat flow is formed between the outer cylindrical metal member **44** and the insulating cylindrical layer **60** and between the insulating layer **60** and the metal ring members **56**. Similarly, a good bond is formed between the inner hollow cylindrical member **42** and the inner cylindrical insulating layer **46** and between the insulating layer **46** and the inner metal ring members **48**. Member **42** is in compressive stress.

After removal of the welded ends, disks, electrical connector clamps **62** and **64** may be then attached to form the thermoelectric device **30**. The device **30** may then be connected to a load **66** by means of electrical leads **68** and **70** attached to terminals **63** and **65** of clamps **62** and **64**.

The inner cylindrical metal member **42** of the device **30** is particularly suited to serve for passing high temperature gases and liquids so as to make this the hot side, and the outer cylindrical metal member of the device can be exposed to the cooling medium to serve as the cold side of a thermocouple. The inner cylindrical member may be conveniently heated by passing hot water, steam, a flame or the like therethrough. The outer cylindrical member may be cooled by flowing water or cold gases or air thereover. The difference in temperature between the hot side and cold sidewall cause an electrical current to be generated in the thermoelectric device by the phenomenon which is known in the art as the Seebeck effect. However, it should be understood that the inner metal member may serve as the cold side and the outer metal member as the hot side.

Furthermore, the Peltier effect may be employed on the device **30** to produce refrigeration or cooling devices by passing electrical current through the leads **68** and **70**.

The preferred embodiment of this device **30** anticipates that in use the member **42** is the high temperature side. Thick wall inner metal member **42** is in compression as a result of processing of the element **40** in autoclave. The thickness of the member **42** is selected so as to enable the member **42** to withstand the temperature and pressure of the autoclave without failure or collapse. The hot pressing of the components of the element **40** at the high temperature and pressure of the autoclave leaves the metal of the thick wall inner member **42** in a state of high compression.

Therefore, when the member **42** is the hot side of the thermoelectric element **40**, the elevated temperature of the high temperature media passing through the hollow causes the member **42** to expand thereby enabling the member **42** to endeavor to remain in a good thermal conductivity relationship with adjoining components of the element **30**.

With reference to FIG. **4** there is shown a thermoelectric element **80** utilizing an alternate embodiment of the teachings of this invention.

The element **80** comprises a thin wall hollow inner cylindrical metal member **82** and a concentric outer cylindrical metal member **84**. Disposed within the hollow inner cylindrical metal member **82** is a suitable solid fuel source **86**.

An insulating hollow cylindrical member **88** is disposed about and joined to the member **82**. The member **88** comprises a material such, for example, as alumina, porcelain, mica and boron nitride. However, the insulating material may be plasma jet sprayed on the outer surface of the inner cylindrical member **82**.

A plurality of inner bridging ring members **90** are disposed about and joined to the insulating member **88**. The ring members **90** are electrically insulated from each other by means of insulating washers **92** and **94** comprising materials such, for example, as mica, or those selling under the trade name of Lavite or Mycalex are alternately disposed between the ring members **90**. The only difference between the washers **92** and **94** is the inside and outside diameter measurements.

A plurality of a first N-type thermoelectric material washer members **96** and a plurality of first P-type thermoelectric material washer members **98** are alternately disposed on and joined to the bridging metal ring member **90**.

A plurality of second N-type thermoelectric material washer members **100** are disposed on, and joined to, the first N-type washer members **96**. A plurality of second P-type thermoelectric material washer members **102** are disposed on, and joined to, the first P-type washer member **98**. The thermoelectric materials selected for comprising the members **96, 98, 100** and **102** are chosen to provide the most efficient source of thermoelectricity for the expected temperature gradient across each member **96, 98, 100** and **102** to be experienced during operation of the element **80**.

The employment of the plurality of two different N-type thermoelectric materials and the plurality of two different P-type thermoelectric materials is a technique variously known as "thermal cascading" or "segmenting." As a specific example of this technique to illustrate this particular embodiment of this invention, the thermoelectric materials may be as follows:

Washer members **96**—an N-type lead telluride alloy embodying a small amount of lead iodide as an additive and commercially available under the trade mark "TEGS–3N."

Washer members **100**—an N-type lead telluride alloy embodying a small amount of lead iodide as an additive and commercially available under the trade mark "TEGS–2N."

Washer members **98**—a P-type lead telluride-tin telluride alloy commercially available under the trade mark "TEGS—3 P."

Washer members **102**—a P-type lead telluride alloy commercially available under the trade mark "TEGS—2P."

Electrically insulating the members **100** from the members **102** from each other is a plurality of insulating washers **104** and **106**, alternately disposed on, and joined to, the corresponding insulation washers **92** and **94**. The washers **104** and **106** comprise the same materials as the washers **92** and **94**.

A plurality of outer bridging metal ring members **108** are disposed on, and joined to, the thermoelectric washer members **100** and **102**, the ring members **108** each contacting a pair of composite P-type thermoelectric washer members **96–100** and P-type thermoelectric washer members **98–102**. The ring members **108** are electrically insulated from each other means of the insulating washer **106**.

A hollow concentric insulating cylindrical member **110** comprising a material such as that employed for reference numerals **88** is disposed about and joined to the outer ring members **108**. The outer cylindrical metal member **84** is disposed about and joined to the insulating cylindrical member **110**.

This alternate embodiment of the teachings of this invention also enables the thin wall of the inner member **82** to be collapsed under the influence of the temperature and the pressure of the autoclave onto the surface of the solid fuel source **86**. The resulting structure therefore enables a good thermal conductivity relationship to be retained between all components of the element **80** during operation of the element **80**.

Although hot isostatic pressing alone will produce a satisfactory thermoelectric device in accordance with the teachings of this invention, it is desirable in many instances to interpose a cold working or a cold compaction processing step between the assembly of the components and the hot isostatic pressing of the components of the device. The purpose of this cold working or compaction process step is to remove substantially all of the assembly clearances and voids from the internal circuit structure of the element prior to exposing the components of the element to the elevated temperatures of the hot isostatic pressing process. This precautionary cold working or compaction step effectively limits the possibility of sublimation of any of the component materials of the element, particularly the thermoelectric materials thereby preventing the resulting transport of the resultant vapors of the sublimed material through clearances and voids in the internal circuit structure and subsequent condensation of the sublimed material vapors at undesirable locations within the structure of the element.

Swagging, rocking-roll tube reducing and isostatic cold compressing are suitable processes for effecting this intermediate process step on the thermoelectric elements. Usually, a specific thermoelectric element is designed mechanically to be compatible with a specific cold working or a cold compaction process. Swagging and rocking-roll tube reducing will yield uniform overall diametral changes at the expense of a slight distortion and/or elongation of the element in an axial direction. Isostatic cold compressing, performed in a liquid or a gas autoclave at about room temperature and applied pressures of from 20,000 p.s.i. to 100,000 p.s.i., will yield uniform diametral changes proportional to the elastic/plastic properties of the material or materials at any given cross-sectional plane along the axis of the element with substantially no attendant axial displacement. The temperatures of this "cold"

pressing step are preferably at about room temperature, 250° C., but obviously can be lower and somewhat higher, up to about 100° C.

The reduction in the annular area between the inner and the outer cylindrical members which results from any of the above-mentioned intermediate cold working process steps is generally less than 10 percent. The percentage reduction of the annular area produced by this cold compacting step renders a small reduction during the hot isostatic pressing of the annular area fully adequate to secure metallurgical bonding, so that the larger reductions in the 1 percent to 15 percent range are unnecessary. Thus, 1 percent to 6 percent hot isostatic reduction will be fully adequate, and in some cases even less than 1 percent is sufficient.

Referring now to Table I there is shown a compilation of data obtained from the fabrication of each of six different types of tubular thermoelectric elements in accordance with the teachings of this invention. Particularly, the data of Table I illustrates the magnitudes of the reduction in the annular cross-sectional area of each element achieved as a result of an intermediate cold working process step, as well as the additional reduction in the annular cross-sectional area achieved as a result of hot isostatic pressing. The cold isostatic pressing and the hot isostatic pressing applied pressure only to the exterior surfaces of the elements.

TABLE I

Element type	Initial dimensions O.D. (in.)	Initial dimensions I.D. (in.)	Cold processing Method	Cold processing O.D. (in.)	Cold processing Reduction in annular area [1]	Hot isostatic pressing Temp. (° C.)	Hot isostatic pressing Pressure (p.s.i.)	Hot isostatic pressing O.D. (in.)	Hot isostatic pressing Reduction in annular area [1]
1 (Example I)	0.870	0.375	Swaging	0.860	2.8	750	10,000	0.840	8.3
2 (Example II)	1.625	0.500	do	1.590	4.7	750	10,000	1.570	7.3
3 (Example IV)	1.700	0.500	Cold compaction at 50,000 p.s.i.[2]	1.675	3.2	650	20,000	1.660	5.1
4	1.700	0.500	None			650	15,000	1.663	4.7
5	2.714	1.093	Cold compaction at 50,000 p.s.i.[2]	2.659	4.8	650	20,000	2.632	7.1
6	1.685	0.752	do [2]	1.652	4.8	650	20,000	1.642	6.3

[1] Percent of initial area.
[2] Cold isostatic compressing.

The following examples are illustrative of the teachings of this invention:

Example I

Six thermoelectric elements similar to that shown in FIG. 3 were assembled and fabricated by employing a prior art method as follows:

The inner cylindrical member employed was a stainless steel hollow tube having a 0.376 in. I.D. and 0.426 in. OD. and having a 0.015 in. thick tube of boron nitride disposed thereon. The bridging contact ring members consisted of low carbon steel and were of two different sizes. The inner contacts measured 0.460 in. I.D. and 0.514 in. O.D. The outer contacts measured 0.76 in. I.D. and 0.79 in O.D. The thermoelectric washers employed consisted of P and N-type lead telluride having a density of 90 percent of theoretical and measuring 0.764 in. O.D. and 0.516 in. I.D. The insulating material between alternate thermoelectric washers and bridging contacts consisted of mica washers and were of two sizes. The inner insulating washers measured 0.764 in. O.D. and 0.460 in. I.D. The outer insulating washers measured 0.788 in. O.D. and 0.516 in. I.D. The outer bridging contacts had a 0.015 in. thick boron nitride tube disposed thereon. The outer cylindrical member consisted of a stainless steel tube 10 in. long and measuring 0.870 in. O.D. and 0.821 in. I.D. The total gap space of the assembly in the radial direction was 0.006 in.

Annular end plugs consisting of sheet stainless steel were then inserted and welded at the ends of the assembly to the inner and outer tubes and the annular area between the inner and outer tubes of the assembly was evacuated through a tube which was then sealed off. The assemblies were each disposed in a separate autoclave and treated in a similar manner. However, autoclave pressure was imposed on both the outer and inner tube surfaces of the assembly. The assemblies were initially under a 10,000 p.s.i. pressure at room temperature, and then heated to a temperature of 650° C. while maintaining the same pressure and they were held at that temperature and pressure for 2 hours. The assemblies were then cooled and the pressure decreased to about 4000 or 5000 p.s.i., the decrease in pressure being linear with the decrease in temperature. The gas pressure maintained in the autoclave was through the use of helium gas.

The devices were tested by inserting a rod heater and thermocouples in each bore. A temperature difference of 168° C. was maintained between the outer and inner cylindrical members when the outer side was cooled with water. The elements were evaluated for normalized thermal conductance and normalized overall efficiency when operated over a period of time. The data obtained from these tests is plotted in FIGS. 5 and 6 and identified as "prior art elements."

Example II

Three thin wall thermoelectric elements hereinafter identified as No. 1, 2 and 3, were prepared and assembled. The basic construction of each element was the same as the element shown in FIG. 3 except that the inner member of each of the elements was of the thin wall hollow tube type and a simulated solid fuel source was employed. Each of the elements was exactly the same as the prior art elements fabricated and tested in Example I except that elements 1, 2 and 3 were fabricated in accordance with the teachings of this invention.

The inner cylindrical member employed was a stainless steel hollow tube having a 0.376 in. I.D. and 0.426 in. O.D. and having a 0.015 in. thick tube of boron nitride disposed thereon. The bridging contact ring members consisted of low carbon iron and were of two different sizes. The inner contacts measured 0.460 in. I.D. and 0.514 in. O.D. The outer contacts measured 0.760 in. I.D. and 0.790 in O.D. The thermoelectric washers employed consisted of P- and N-type lead telluride having a density 90 percent of theoretical and measuring 0.516 in. I.D. and 0.764 in. O.D. The insulating material between alternate thermoelectric washers and bridging contacts consisted of mica washers and were of two sizes. The inner insulating washers measured 0.460 in. I.D. and 0.764 in. O.D. The outer insulating washers measured 0.516 in. I.D. and 0.788 in. O.D. The outer bridging contacts had a 0.015 in. thick boron nitride tube disposed thereon. The outer cylindrical member consisted of three sections of stainless steel tube totaling 10 in. in length and measuring 0.821 in. I.D. and 0.870 in. O.D. The total gap space of the assembly in the radial direction was 0.006 in.

The outer bridging contact at each end contained a flange into which four steel conductor pins were inserted. These pins passed through tubular blocks of electrically insulating material comprising aluminum magnesium silicate and a stainless steel retaining ring. The pins were insulate from the retaining ring with small tubular washers of boron nitride. At each end of the devices a stainless steel end ring containing an evacuation tube was welded to the inner and outer cylindrical members. The joints between the three sections of the outer cylin-

drical member were welded together such that joints were also formed between the outer cylindrical member and the retaining rings. The annular region between the inner and outer cylindrical members was then evacuated through the evacuation tubes and the tubes were then sealed by welding.

Rod-type electrical resistance heaters measuring 0.375 in. O.D. and 3.25 in. long were inserted in the bores of the assembled elements such that the heater length was adjacent to the active thermoelectric circuit. The remainder of the bore was filled with solid plugs of insulating material comprising aluminum magnesium silicate. A stainless steel solid plug was then welded into each end of the bore of the inner cylindrical member.

The elements so sealed were then passed through the dies of a swaging machine, reducing the O.D. of the element from 0.870 to 0.860 in. This represents a reduction in annular cross-sectional area of about 2.8 percent, and effectively placed all of the layers in physical contact with one another.

The elements were then disposed in an autoclave. The autoclave was heated with an internal electric furnace and pressurized by employing helium gas. A pressure of 7500 p.s.i. was imposed on the elements at room temperature. They were then simultaneously heated and additionally pressurized until a temperature of 650° C. and a pressure 10,000 p.s.i. were reached. These conditions of temperature and pressure were maintained for 2 hours, after which the temperature and pressure were simultaneously reduced until room temperature and a pressure of about 5000 p.s.i. were reached. The remaining pressure was then removed and the elements were taken out of the autoclave. The O.D. of the elements had been reduced to 0.840 inch, which represents an annular area reduction of about 5.7 percent from the preautoclave condition and a total annular area reduction of about 8.3 percent from the preswaging condition.

The ends of the devices were machined to expose the conductor pins of the thermoelectric circuit and the terminals of the rod heater. Testing was accomplished using the rod heater and an external blower. A temperature difference of 168° C. was maintained across the radius of each device by heating the inner cylindrical member with the rod heater and cooling the outer cylindrical member with the forced air form the blower.

The elements were evaluated for normalized thermal conductance and normalized overall efficiency when operated over a period of time. The data obtained are graphed as shown in FIGS. **5** and **6**. The superiority in the performance of elements **1**, **2** and **3** is clearly evident and can be attributed solely to the novel fabrication process of this invention.

Example III

Two thick wall thermoelectric elements, hereinafter identified as elements No. 4 and **5**, were assembled. The basic construction of each element was similar to that shown in FIG. **3**.

The inner cylindrical member was a Hastelloy B hollow tube having a 0.500 in. I.D. and 0.650 in. O.D. and having a 0.018 in. thick tube of boron nitride disposed thereon. The bridging contact ring members consisted of low carbon and and were of two different sizes. The inner contacts measured 0.690 in. I.D. and 0.791 in. O.D. The outer contacts measured 1.291 in. I.D. and 1.330 in. O.D. The thermoelectric washers employed consisted of P- and N-type lead telluride having a density 93 percent of theoretical and measuring 0.792 in. I.D. and 1.290 in. O.D. The insulating material between alternate thermoelectric washers and bridging contacts consisted of mica washers and were of two sizes. The inner insulating washers measured 0.690 in. I.D. and 1.289 in. O.D. The outer insulating washers measured 0.793 in. I.D. and 1.330 in. O.D. The outer bridging contacts had a 0.020 in. thick boron nitride tube disposed thereon. The outer cylindrical member consisted of three sections of stainless steel tube totaling 14.4 in. in length and measuring 1.374 in. I.D. and 1.625 in. O.D. The total gap space of the assembly in the radial direction was 0.006 in.

The outer bridging contact at each end contains a flange into which four steel conductor pins are inserted. These pins pass through tubular blocks of insulating material comprising magnesium aluminum silicate and a stainless steel retaining member. The retaining member was welded to the inner cylindrical member. The pins were insulated from the retaining member with small tubular washers of boron nitride. At each end of the elements a stainless steel end ring containing an evacuation tube was welded to the inner and outer cylindrical members. The joints between the three sections of the outer cylindrical member were welded together such that joints were also formed between the outer cylindrical member and the retaining members. The annular region between the inner and outer cylindrical members was then evacuated through the evacuation tubes and the tubes were then sealed by welding.

The elements were then passed through the dies of a swaging machine, reducing the O.D. from 1.625 to 1.590 in. This represents a reduction in annular cross-sectional area of about 4.7 percent and effectively eliminated internal clearances and placed all the layers in close contact with one another. A stainless steel of solid plug was then welded into each end of the bore of the inner cylindrical member of each device.

The devices were then disposed in an autoclave which could be pressurized with helium gas and heated with internal coils. A pressure of 7500 p.s.i. was imposed on the elements at room temperature. They were then simultaneously heated and additionally pressurized until 750° C. and 10,000 p.s.i. were reached. These conditions were maintained for 2 hours, after which the temperature and pressure were simultaneously reduced until room temperature and about 7500 p.s.i. were reached. Then the remaining pressure was removed and the elements were taken out of the autoclave. The outside diameter of the elements had been reduced to 1.570 inch, which represents an area reduction of about 2.8 percent from the preautoclaving condition and a total area reduction of about 7.3 percent from the preswaging condition.

The ends of the elements were machined to expose the conductor pins of the thermoelectric circuit and to remove the plugs from the bores of the inner cylindrical members.

Testing was accomplished by inserting a rod heater in the bore to heat the inner surface and using forced air from a blower to cool the outer surface. A temperature difference of about 450° C. was maintained across the radius of the devices in this manner.

The elements were evaluated for normalized thermal conductance and normalized overall efficiency when operated over a period of time. The data obtained are plotted on a graph as shown in FIGS. **5** and **6**, as elements No. **4** and 5.

Example IV

A thick wall thermoelectric element identical to those elements fabricated and described in Example III, except for having an inner cylindrical member made of Inconel X-750 and an outer cylindrical member measuring 1.700 in. O.D., was assembled, evacuated, and the ends hermetically sealed by welding. This element is described hereinafter as element No. **6**.

Along, close-fitting solid stainless steel center rod and two short solid stainless steel end plugs, all closely fitting the bore were inserted as a solid column into the bore of the inner cylindrical member and the end plugs were seal welded to the ends of the member. The element was then cold isostatic compressed in a liquid autoclave at room temperature, with an isostatic pressure of 50,000 p.s.i. being applied to the exterior surfaces of the element only. This cold isostatic compression process reduced the outer diameter from 1.700 to 1.675 inches, which represented a reduction in annular cross-sectional area of about 3.2 percent, and effectively placed all the layers of the element in an intimate physical contact with one another.

The thermoelectric element was then disposed within an autoclave which could be pressurized with helium gas. The au-

toclave was heated internally with electrical coils. While at room temperature helium at a pressure of 15,000 p.s.i. was imposed on the exterior surfaces of the element only. The element was then simultaneously heated and the pressurized increased until the conditions of temperature of 650° C. and a pressure of 20,000 p.s.i. were reached. The elevated temperature and higher pressure were maintained on the element for 2 hours, at which time the temperature and the pressure were simultaneously reduced until the helium was at room temperature and a pressure of 15,000 p.s.i. was achieved. The helium gas was released from the autoclave and the processed element removed from the autoclave.

The outside diameter of the element had been reduced to 1.660 inches which represented an annular area reduction of about 2.0 percent from the prehot isostatically compressed condition, there being a total annular area reduction of about 5.1 percent from the precold compaction condition.

The element was prepared for testing, tested and the results evaluated in a similar manner as the elements of Example III. The data obtained from the tests is plotted in FIGS. **5** and **6** and denoted as element No. **6**.

A review of the data plotted in FIG. **5** reveals that the element utilizing and fabricated by means of the teachings of this invention are far superior to those elements manufactured by the prior art method.

It is to be noted that the elements embodying the teachings of this invention still have a normalized thermal conductance of 0.95 of the original values or better after 900 hours of operating time. In the elements embodying the teachings of the prior art the normalized thermal conductance deteriorated to below 0.7 after less than 600 hours of operating time.

In reviewing the collected data plotted in FIG. **6**, it will be seen that the elements embodying the teachings of this invention have a higher normalized efficiency for a greater operating time than the elements embodying the teachings of the prior art. After 600 hours of operating time the elements embodying the teachings of this invention dropped to a normalized overall efficiency of approximately 0.9 of the initial values and remained at this efficiency for more than 300 hours more. By comparison the prior art processed elements decreased to an efficiency of from approximately 0.6 to 0.85 in 500 hours of operating time or less.

While the invention has been described with reference to particular embodiments and examples, it will be understood, of course, that modifications, substitutions and the like may be made therein without departing from its scope.

We claim as our invention:

1. In a process for producing an integral thermoelectric element comprising a hollow inner cylindrical member, a concentric outer cylindrical member and a body of thermoelectric material disposed in the compartment defined by the outer surface of the inner member and the inner surface of the outer member, the steps comprising:

1. disposing the body of thermoelectric material in the compartment between the inner and the outer member,
2. sealing the ends of the compartment and the hollow of the inner member so that no fluid may enter therein,
3. evacuating the sealed body of thermoelectric material in the compartment,
4. compressing the members and the thermoelectric material at a temperature from about 250° C. to slightly below the melting temperature of the lowest melting material comprising the element by applying an isostatic pressure of from 5,000 p.s.i. to 50,000 p.s.i. only to exterior surfaces of the element until the element has been plastically deformed at its exterior surfaces and reduced in cross-sectional area by a value of from about 1 percent to 15 percent to provide at least an intimate physical contact between the body of thermoelectric material and the inner and outer members, and the inner cylindrical member is in compression after the isostatic pressure is removed.

2. The process of claim **1** in which compressing the members results in a metallurgical bond between the body of thermoelectric material and the inner and outer members of the element.

3. The process of claim **1** in which the hollow inner cylindrical member has a thin wall, sealing and evacuating a solid heat source disposed within the hollow of the inner member, and collapsing the thin wall upon the solid heat source by the application of the isostatic pressure at the elevated temperature.

4. The process of claim **1** including cold working the components comprising the element after assembly to reduce internal clearances and close gross voids prior to being subjected to the isostatic pressure at an elevated temperature.

5. The process of claim **4** in which the cold working is performed by isostatic pressure applied only to the exterior surface of the assembled components at room temperature.

6. The process of claim **1** in which the hollow of the inner member is filled with an inert gas and sealed prior to the assembled element being subjected to the isostatic pressure at an elevated temperature.

7. In a process for producing a thermoelectric element, the steps comprising:

1. disposing a plurality of inner bridging metal ring members on an insulated hollow cylindrical metal member, the ring members being electrically insulated from each other,
2. disposing a plurality of washers of thermoelectric material on the ring members,
3. disposing a plurality of outer bridging metal ring members on said thermoelectric washers, the ring members being electrically insulated from each other, disposing an insulated outer cylindrical metal member on the ring members, the assembly having a gap space of not above about 1 percent of the diameter of the outer cylindrical member,
4. sealing the ends of the cylindrical metal members to provide a sealed enclosure for the components therein,
5. sealing the end of the hollow cylindrical metal member so that no fluid can enter therein,
6. evacuating the internal spaces within the sealed assembly, and
7. compressing the members and the components contained therebetween at a temperature of from 250° C. to slightly below the melting temperature of the lowest melting temperature component in the assembly by applying an isostatic pressure of from 5,000 p.s.i. to 50,000 p.s.i. to the exterior surface only of the assembly until plastic deformation occurs at the outer portions and until there is a reduction in cross-sectional area of the space between the inner and outer cylindrical members of from 1 percent to 15 percent whereby to provide a metallurgical bond between the bridging metal ring members and the thermoelectric washers so that an applied or induced electric current will meet a low electrical resistance flow between said washers, and the element in use at elevated temperatures maintains a high electrical and thermal conductivity.

8. The process of claim **7** including:

cold working the assembled members and components of the element prior to compressing the members and the components isostatically at an elevated temperature to reduce internal clearances within the element.

9. The process of claim **8** in which cold working is performed by isostatic pressure on exterior surfaces only of the element at about room temperature.

10. The process of claim **7** in which the hollow inner cylindrical member has a thin wall, sealing and disposing a solid heat source disposed within the hollow of the inner member, and collapsing the thin wall upon the solid heat source by the application of the isostatic pressure at the elevated temperature.

11. The process of claim **7** in which the hollow of the inner

member is filled with an inert gas and sealed prior to the assembled element being subjected to the isostatic pressure at an elevated temperature.

12. The process of claim 7 in which each of the washers of thermoelectric material comprise at least two different varieties of the same type thermoelectric material each variety of thermoelectric material having an optimum range of thermoelectric efficiency different from each of the other varieties, one variety of one type thermoelectric material comprising one radial portion of the washer and second variety said one type thermoelectric material comprising the second radial portion of the washer.

13. The process of claim 9 in which the washers of thermoelectric comprise at least two varieties for each type of thermoelectric material each variety having of same type thermoelectric material having an optimum range of thermoelectric efficiency different from each of the other varieties, one variety of one type thermoelectric material comprising one radial portion of the washer and a second variety of said one type thermoelectric material comprising the second radial portion of the washer.