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[54] ISOTOPIC THERMAL POWER SOURCE

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[63] Continuation of Ser. No. 624,587, March 20, 1967, abandoned.

[52] **U.S. Cl.** .....**29/182.5**, 75/206, 176/69, 252/301.1 R, 264/.5

[51] **Int. Cl.** **B22f 1/00**

[58] **Field of Search** 75/206; 29/182.5; 176/69, 89; 264/.5; 252/301.1, 517, 426

[56] **References Cited**

UNITED STATES PATENTS

3,154,501	10/1964	Hertz	252/301.1
3,421,001	1/1969	Fitzgerald et al.	252/301.1
3,470,030	9/1969	Lindholm et al.	75/202
2,767,463	10/1956	Tacvorian	29/182.5
3,073,698	1/1963	Arbiter	264/.5 X
3,096,263	7/1963	Kingston et al.	176/69
3,161,504	12/1964	Black et al.	29/182.5 X
3,236,922	2/1966	Isaacs et al.	252/301.1 X
3,346,673	10/1967	Last et al.	264/.5
3,348,943	10/1967	Pollock	264/.5 X

OTHER PUBLICATIONS

Young, Cobalt, Reinhold Publishing Corp., 1948, pp. 106–107.

Kirby et al., Promethium Compatibility and Encapsulation Studies BNWL–SA–488; CONF–660305–2; 12–27–65.

Hampel, Rare Metals Handbook, Reinhold Publishing Corp., 1961, pp. 134.

Nuclear Science Abstracts, Vol. 19, No. 14, 7–31–65.

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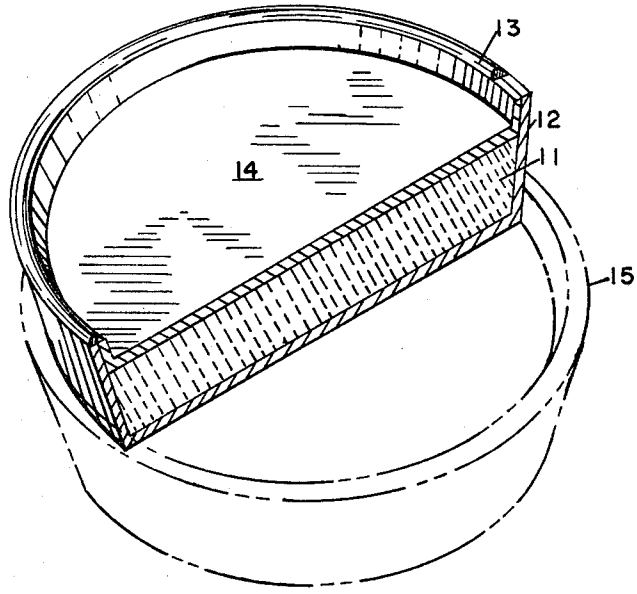
[57] **ABSTRACT**

An isotopic thermal power source is formed having good heat conductivity and desired ductility by utilizing a mixture of molecules of a metal refractory or ceramic compound and metal with the metal of said refractory compound and the metal atoms being capable of being activated to radioactive forms or being in radioactivated forms. Preferably the metal refractory is thulium oxide and the metal is thulium. Thulium 169 is capable of being activated to thulium 170 and/or thulium 171 to produce heat sources comprising the mixture having power ratings of at least 0.5 thermal watts per cubic centimeter.

10 Claims, 1 Drawing Figure

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ISOTOPIC THERMAL POWER SOURCE

This application is a continuation of Ser. No. 624,587, filed Mar. 20, 1967, now abandoned.

BACKGROUND OF THE INVENTION

There has been an increasing demand for radioactive heat sources for energy purposes which are used in thermionic and thermoelectric devices such as thermoelectric generators. Heretofore, attempts have been made to provide such heat sources by the fabrication of radioactive isotope capsules or wafers that are normally incorporated into such devices as energy sources. When ceramic or refractory forms of radioactive isotopes are used, some problems are encountered due to limited heat conductivity of the ceramics or refractories which limits heat transfer from within fuel capsules or forms and thus causes excessive temperatures at the center of the heat source. On the other hand, when pure metal is used as the radioactive isotope, low melting temperatures as compared to the refractory or ceramic forms are encountered which are not acceptable for some purposes. In addition, handling of substantially metallic forms of the radioactive isotopes is sometimes difficult particularly in the case of thulium metal.

Even though thulium oxide has a relatively high thermal conductivity, the thermal conductivity of oxides, ceramics, refractories and the like are characteristically lower than the metals. However, since thulium oxide has so many desirable properties such as its very high melting point, its stable lattice structure and its high commercial purity, it is desirable to devise a method of increasing the thermal conductivity of thulium oxide sintered or high density ceramic forms to enhance the utility of this material as a radioisotopic heat source in the form of thulium oxide 170 or thulium oxide 171.

As described in the patent application of Joseph J. Fitzgerald et al. Ser. No. 352,725, filed Mar. 16, 1964, in the United States Patent Office and issued on Jan. 7, 1969 as U.S. Pat. No. 3,421,001, ceramic wafers of thulium oxide are known. However, there is some possibility of melting in the center of large fuel assemblies made from such ceramic wafers with attendant associated problems when such wafers are used as heat sources. Therefore, an improved fuel form would consist of a fuel assembly with the virtues of the Fitzgerald invention above, including high power density,but with higher thermal conductivity than Tm_2O_3.

SUMMARY OF THE INVENTION

According to the invention, an isotopic thermal power source is preferably made by forming a cold mixture of molecules of a metal refractory or ceramic compound and a metal with the metal atoms of both the pure metal and the metal of the compound being capable of activation to radioactive isotopic forms. The metal and metal refractory compound are preferably homogeneously mixed with the metal comprising from 10 to 80 percent by weight of the mixture and the metal refractory from 90 to 20 percent by weight of the mixture. After the mixture is formed, it is preferably treated to form cold wafers, i.e., non-radioactive, which can be sintered, pressed or extruded using known techniques as described in the aforementioned Fitzgerald et al. U. S. patent application. The cohesive isotopic forms are later activated to form a radioactive isotope thermal power source having a power rating of preferably at least 0.5 watts per cubic centimeter.

Preferably the metal is thulium and the metal refractory is thulium oxide with the thulium being thulium 169. The mixture can then be activated to thulium 170, thulium 171 or a suitable mixture of the two depending upon the power requirements desired.

BRIEF DESCRIPTION OF THE DRAWING

The FIGURE is a diagrammatic showing of a preferred embodiment of a radioactive isotopic thermal fuel assembly of this invention.

PREFERRED EMBODIMENT OF THE INVENTION

Preferably thulium and thulium oxide are used in the mixture since thulium has a relatively high thermal neutron cross section and thulium can be encapsulated prior to neutron exposure in such a manner that the encapsulation contains a stable material in a form essentially inactive and safe for handling. Thus "hot" or radioactive material need not be handled in the fabrication process but, inert or "cold" material can be processed and later activated in conventional reactors and the like. Thulium oxide is a preferred thermal power source prepared as thulium 169 and later converted to thulium 170 and/or thulium 171 partly because it is the only stable isotope of thulium (100 percent abundant) and has a thermal neutron cross section of approximately 118 barns which assures a sufficient activation to thulium 170, or with neutron fluxes in the range of 2 to 5×10^{15}n/cm^2/sec., suitable and desirable quantities of thulium 171 can be induced into the thulium oxide wafer or other form. When thulium oxide is used alone, heat transfer properties may not reach desired levels. Therefore, thulium metal atoms are included in a mixture to increase thermal conductivity.

The thulium is preferably used in amounts of from 10 to 80 percent by weight of the mixture and molecules of thulium oxide compound are preferably used in amounts of from 90 to 20 percent by weight of the mixture. The specific amount of thulium will vary depending upon the properties wanted in any particular application. For high ductility and less frangibility of a resulting ceramic or cohesive form, higher amounts of metal are used as would be the case if higher heat conductivities are desired. Similarly, where less ductility and heat conductivity are needed, and particularly where the highest melting points are desired, smaller amounts of metal can be used in the mixture.

The cold forms of the power sources of the present invention can be made by mixing finely powdered thulium oxide 169 with powdered thulium 169 metal. The thulium oxide can be obtained by conventional means where rare earths are separated from ore and then from each other in an ion exchange column. The thulium is eluted out in bands and reduced to thulium oxide to form a fine white powder anywhere from 98 to 99.99 percent pure. Preferably, the thulium and thulium oxide are uniformly mixed together and then formed into ceramic or refractory wafers, discs and the like in accordance with known procedures.

In still another method, thulium oxide alone can be used as a starting material and a portion of the thulium oxide is reduced to form a thulium metal with

uniformly distributed thulium metal atoms within the thulium oxide mass. For example, thulium oxide can be heated and pressed to sintering in a vacuum or reducing atmosphere yielding a resultant mixture of thulium metal atoms and thulium oxide molecules in a unitary capsule or wafer. A conventional vacuum chamber having enclosed heating elements can be used starting with thulium oxide and admitting a reducing agent during heating with or without pressing. Reducing agents such as hydrogen gas are suitable. The presence of thulium metal is evidenced by the change in the uniform fine white powder or with a yellow-green cast of thulium oxide to a mixture of this appearance with darker color resulting in an over-all greyish color indicating the presence of thulium metal.

The thulium metal when dispersed in the matrix of thulium oxide has little physical effect on the structure other than increasing ductility and thereby reducing frangibility. The metal atoms are surrounded by oxide molecules and do not act as a substantial contributor to the strength of the matrix at high temperatures but do contribute to increase thermal conductivity and ductility. Preferably the thulium metal and thulium oxide are homogeneously admixed in the final product.

In forming the ceramic-metallic wafers of this invention, it is also possible to have the core portion of the wafer of a higher metallic content than the surface in order to assure the high melting point of the surface of the radioisotopic fuel wafer and to provide the highest thermal conductivity possible in the central portions and yet to attain the highest achievable power density in the completed fuel form. This can be accomplished by the invention by initially blending a metallic-rich mixture of metallic and refractory ceramic powders and then, during the sintering stage of processing, a strongly oxidizing atmosphere can be used to oxidize the surface exposed metallic portions of the mixture, thus yielding a metal-rich core in a ceramic bounded wafer.

Typical wafers formed from mixtures of thulium and thulium oxide could for example have a thickness of from 2 to 5 millimeters and a diameter of from one-fourth inch to 2½ inches although the dimensions of such wafers can vary greatly depending upon the ultimate use.

Preferably the thulium and thulium oxide mixture is compacted to as near to its theoretical density as possible in order to increase power output efficiency since the maximum power per unit dimension is a function of density of thulium atoms. In order to achieve maximum power density, it is desirable to compress the thulium oxide and thulium mixture to a density of at least 80 percent of its theoretical maximum density, and most preferably to a range of 90 to 95 percent of theoretical density. Preferably wafers are formed by compressing the thulium oxide and thulium powder mixture utilizing conventional equipment at an elevated temperature in the range of from just below the melting temperature of thulium oxide which is in the range of approximately 2,300°C to 2,600°C to above the melting temperature of thulium which is often considered to be approximately 1,900°C.

When a mixture of thulium and thulium oxide is used, an inert atmosphere is preferably employed during the sintering or ceramic forming step to preserve the percentage of metal as compared with metal oxide in the resultant product. As previously described, when thulium oxide is used as the starting material, a reducing atmosphere is used to convert some of the metal of the compound to thulium metal.

In a specific example of this invention, a mixture of 20 percent by weight powdered thulium 169 metal and 80 percent by weight thulium oxide 169 is formed by uniformly mixing. The resulting mixture is then compressed in a hydraulic press at a pressure of about 1,000 pounds per square inch and thence sintered in an inert atmosphere at a temperature of 2,000°C to form a ceramic wafer as indicated in the FIGURE showing the mixture at **11**. The wafer **11** is then sealed in casings **12** and **14** of about 0.002 inch thick molybdenum by electron beam welding the enclosure at **13**. The wafer is later neutron activated for 30 days at a flux of 1×10^{15}n/cm^2/sec to produce thulium 170 and 171 in the wafer. The resultant activated wafer is an ideal thermal fuel source for a thermoelectric generator, has low frangibility, and high thermal conductivity yielding a power output of about 18 thermal watts per cubic centimeter.

In accordance with known procedure, the thulium oxide wafers or other ceramic forms made can be placed in and secured to casings as is well known in the art. Preferably the casing material has a high melting point which is at least in excess of the melting point of the material contained within it. The casing material should not be conducive to significant activation and therefore, it should have a very low cross section for absorption of thermal neutrons and any neutron activation products should have a short half life. Preferably, the casing materials should be of material having a thermal neutron cross section of less than 0.2 barns and a half life of less than 3 days. The casing material should not react with the fuel material or isotope which forms a wafer. It has been found that molybdenum is a preferred material for casings although other materials such as zirconium, tantalum and tungsten are also useful. Such encapsulations are preferably fabricated cold, i.e., not radioactive, and require no shielding and may be handled as inactive materials.

In accordance with known procedures, the encapsulations can later be activated for periods preferably of not less than 5 days and not more than 100 days exposed to a flux equal to or greater than 1×10^{14}n/cm^2/sec for production of thulium 170. For production of thulium **171**, the cold forms are exposed to a flux in the order of 2×10^{15}n/cm^2/sec for a period of from 30 to 700 days. The parameters for activation of thulium **169** mixtures in accordance with this invention are the same as those disclosed with relation to thulium oxide 169 in the above-mentioned Fitzgerald et al patent application.

While specific embodiments of this invention have been described, it should be understood that many variations are possible. For example, while thulium and thulium oxide are the preferred components of the mixture, cobalt and its oxide, plutonium and its oxide, polonium and its oxide, promethium and its oxide or mixtures of any metal isotope with another metal isotope in compound form capable of being neutron activated can also be used with the metals of the mixtures increasing thermal conductivity and ductility of result-

ing ceramic or refractory forms. The metals and metal compounds can be formed into mixtures after they have been individually neutron activated. The wafers of ceramic or refractories can be made from the mixtures by sintering,hot pressing, or extruding in accordance with known techniques for fabricating ceramic forms for use as radioactive power sources or other radioactive sources. In some cases, mixtures of thulium 170 metal and thulium oxide 170 or other radioactive isotope forms with their radioactive isotope oxides can be made after activation and then fabricated into a ceramic or refractory form although the handling and fabrication techniques are more complicated. In such cases, the resulting ceramic or refractory forms still exhibit higher thermal conductivity and increased ductility as opposed to the oxide forms when used without metal uniformly and homogeneously incorporated therein.

In view of the many modifications possible, this invention is to be limited only by the spirit and scope of the appended claims.

What is claimed is:

1. A radioisotopic thermal power source having good heat conductivity consisting essentially of a mixture of a thulium refractory oxide and thulium metal said thulium of said oxide compound and said thulium metal being radioactive, said mixture having a power density greater than 0.5 watts/cc.

2. A thermal radioisotopic power source in accordance with claim 1 wherein said thulium oxide is present in an amount of from about 90 to 20 percent by weight and said thulium metal atoms are present in an amount of from about 10 to 80 percent by weight.

3. A thermal power radioisotopic source in accordance with claim 2 wherein a mixture of non-radioactive thulium and non-radioactive thulium oxide is sintered into a cohesive unit prior to irradiation to form radioactive isotopes of thulium from said thulium oxide and said thulium.

4. A thermal power radioisotopic source in accordance with claim 3 wherein said thulium is in the form of thulium 170 and thulium 171.

5. A radioisotopic thermal power source having a power rating of at least 0.5 watts per cubic centimeter consisting essentially of a substantially uniform mixture of from about 10 to about 80 percent by weight thulium metal and from about 90 to about 20 percent by weight of thulium oxide.

6. A radioisotopic thermal power source in accordance with claim 5 wherein said source is in a sintered form.

7. A non-radioactive form capable of being irradiated to form a radioisotopic thermal power source having a power rating of at least 0.5 watts per cubic centimeter,

said form consisting essentially of thulium oxide and thulium metal, said thulium metal and thulium metal of said oxide compound being capable of conversion to radioactive isotope forms.

8. A non-radioactive form in accordance with claim 8 wherein said thulium metal is present in amounts of from about 10 to about 80 percent by weight and said thulium oxide is present in amounts of from about 90 to 20 percent by weight of said mixture.

9. A non-radioactive form in accordance with claim 8 comprising a substantially homogeneously sintered mass.

10. A non-radioactive form in accordance with claim 8 comprising a sintered mass which has a greater concentration of oxide ceramic material in the surface regions formed by sintering the mass in an oxidizing atmosphere.

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