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Fig. 3

Fig. 4

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Fig. 5
**Fig. 6**

- S/\rho /\text{OPTIMIZATION PARAMETER,} \times 10^{-6} \text{watt/cm}^2\text{K}\text{C}

- Temperatures, °C

- 1. 7Zr-93ZrO₂
- 2. 6.5Zr-93.5ZrO₂
- 3. 8Zr-92ZrO₂
- 4. 75Zr-92.5ZrO₂
- 5. 6Zr-94ZrO₂
- 6. 9Zr-91ZrO₂

**Fig. 7**

- Dimensionless Figure of Merit, Z₁
- Thermal Conductivity (K), cal/sec·cm·°C

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ZIRCONIA-BASED THERMoeLECTRIC COMPOSITIONS

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Fig. 8

Fig. 9

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Fig. 12

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ABSTRACT OF THE DISCLOSURE

A thermoelectric element comprising a densified body having electrical leads at opposed portions of said body which comprises a matrix of zirconia and a metal selected from zirconium, titanium, vanadium, and yttrium, a dispersion of said selected metal in said matrix, and a metal oxide selected from yttria, calcia, and a 4% rare earth oxide, when added to said matrix serves to stabilize the zirconia in the crystalline habit.

BACKGROUND OF THE INVENTION

The invention described herein was made in the course of, or under a contract with the U.S. Atomic Energy Commission.

The present invention relates to thermoelectric compositions capable of direct conversion of heat to electricity and to methods of fabricating said compositions. More particularly, the invention relates to thermoelectric compositions which can generate electric power directly from a source of heat at temperatures in the range 1000° C. to 2200° C. over a differential in temperature of from 50° C. to as much as 500° C. between hot and cold junctions. As conducive to a clearer understanding of this invention, reference will be made to a thermoelectric merit factor defined as the relationship $S^{2}/p\kappa$ where $S$ is the Seebeck coefficient, $p$ is electrical resistivity, and $\kappa$ is thermal conductivity. The higher the $S$ factor, the greater the amount of power generation that can be developed from a thermoelectric material for a given energy throughput. The higher the Seebeck coefficient, the higher the merit factor when the product of resistivity and conductivity remains constant. Similarly, the lower the product of the resistivity and thermal conductivity, the higher the merit factor at a given Seebeck coefficient. It is thus seen that the usefulness of a thermoelectric material is related not only to its Seebeck coefficient but also to its electrical and thermal conductivity.

Another object is to provide methods for the fabrication of such compositions.

SUMMARY OF THE INVENTION

The thermoelectric compositions of this invention in their useful state consist of an article of manufacture as a shaped body, comprising a matrix of zirconia and a metal selected from zirconium, yttrium, titanium, and vanadium, a dispersion of said selected metal in said matrix and a metal oxide selected from yttria, calcia, and a 4% rare earth oxide (having an atomic number from 58–71) which, when added to said matrix serves to stabilize the zirconia in the crystalline habit. The amount of metal dispersed in the zirconia matrix should be such that it does not exceed its solubility limit at the intended operating temperature. Above its solubility limit, the metal will tend to precipitate at grain boundaries and migrate to surfaces eventually forming an electrical short circuit between hot and cold junctions. In this context, the solubility limit for zirconium in zirconia should not exceed 20 weight percent zirconium.

We have found that by varying the concentration of the selected metal in the dispersed phase within the above described limits, thermoelectric materials can be produced which exhibit high Seebeck coefficients, low electrical resistivity, and low thermal conductivity to yield sufficiently high energy merit factors to signify their effective utility to generate electrical power at temperatures of at least 1000° C. to 2000° C. and above. The zirconia-based materials are therefore useful in power generation devices associated with missiles, nuclear reactors, chemical reactors, and solar imaging devices where such high temperatures are experienced.

The individual thermoelectric generating unit may take several standard forms. Each unit is comprised of the basic thermoelectric compositions as a cylinder bonded to concentric outer and inner layers of an electrical lead material which is chemically and physically stable at the intended service conditions. Another modification is to join plates or wafers of the zirconia-based element to electrically conducting contacts in a sandwich-type configuration.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings show various embodiments and examples of the invention and data illustrative of the claimed thermoelectric compositions. FIG. 1 shows the effect of electrical resistivity of $Y_2O_3$ stabilized zirconia compositions by varying the $Y_2O_3$ content at relatively constant zirconium content as a function of temperature. FIG. 2 shows the effect on electrical resistivity of $Y_2O_3$ stabilized zirconia compositions by varying the zirconium content at relatively constant $Y_2O_3$ content as a function of temperature. FIG. 3 shows how the Seebeck coefficient in microvolts/° C. varies with concentration of Zr as a dispersed phase in a matrix of $ZrO_2$ and $Y_2O_3$ as a function of temperature. FIG. 4 shows how the Seebeck coefficient varies as a function of temperature in CaO and $Y_2O_3$ stabilized $ZrO_2$ compositions with yttrium titanium, and vanadium as the dispersed metal phase. FIG. 5 shows the effect of adding a stabilizing oxide as a dispersed phase in a representative thermoelectric composition of this invention as a function of temperature. It will be noted that the heating and cooling curve for a dispersion of zirconium in $ZrO_2$ undergoes considerable hysteresis as its crystalline structure changes from one habit to another. By contrast, the heating and cooling curves are identical for a composition containing the stabilizing oxide $Y_2O_3$.

FIG. 6 shows the optimization parameter $S^2/p$ of several thermoelectric compositions, consisting of dispersions of zirconium metal in a zirconia matrix. For purposes of comparison the optimization parameter of a preferred thermoelectric composition consisting of a dispersion of 12 weight percent Y$_2$O$_3$ and 8 weight percent Zr in a matrix of ZrO$_2$ is shown, all as a function of temperature. FIG. 7 shows (1) the variation in a dimensionless figure of merit $ZT$ where $Z$ is the thermoelectric merit factor and $T$ is temperature in ° C. of a preferred thermoelectric composition (consisting of 12 Y$_2$O$_3$–80 ZrO$_2$–8 Zr) as a function of temperature, and (2) the variation in thermal conductivity of said composition as a function of temperature. This composition is termed the preferred composition because it represents the highest measured.
FIG. 8 shows the variation of Seebeck coefficient with temperature in two ZrO_{2}-Zr metal compositions stabilized with 6 percent CaO in one case and 6.5 percent in another. FIG. 9 shows the optimization parameter S^2/ρ of the two thermoelectric compositions of FIG. 8 as a function of temperature. For purpose of comparison, the optimization parameter for the preferred thermoelectric composition consisting of 12 Y_{2}O_{3}-8 ZrO_{2} and 8 Zr is also shown.

FIG. 10 shows the variation in electrical resistivity of three representative ZrO_{2}-based thermoelectric compositions containing CaO as the cubicle stabilizer in two cases and equal quantities (6 percent) CaO and CaO in the third case. In the first case the dispersed metallic phase consisted of 9 percent Zr; in the second case equal amounts (4 percent) of Zr and Ti were used; and in the third case the dispersed metal consisted of 8.5 percent Zr.

FIG. 11 shows the electrical resistivity of the three compositions of FIG. 10 as a function of temperature.

FIG. 12 shows the optimization parameter of three Y_{2}O_{3}-ZrO_{2}-Zr thermoelectric compositions as a function of temperature at varying concentrations of zirconium. These curves show the superiority of the preferred composition (containing 8 percent Zr) over compositions containing higher and lower bircium concentrations.

The zirconia-based thermoelectric compositions of this invention can be fabricated by casting or powder metallurgical methods. Casting is effected by mixing the materials in the proportions desired in a tantalum crucible and fused in an inert atmosphere above 2600° C. In another method process a powdered mixture of zirconia, stabilizing oxide, and metal is blended and then isostatically pressed at about 50,000 p.s.i. in rubber bags. The resultant green strength structures are then sintered at a temperature at least equal to two-thirds of the melting point of the composition. A third method is by hot pressing a powdered mixture of the components in vacuum or inert gas above 1850° C. followed by sintering at a higher temperature. Sintering above 2400° C. for about 2 hours is preferred in order to obtain densities above 95% of theoretical and to obtain a uniform dispersion of the selected metal throughout the zirconia matrix. Sintering below 2200° C. results in heavy grain boundary precipitates which migrate to the surface of the material upon subsequent heating or cooling.

The thermoelectric compositions made in accordance with the foregoing procedures are then machined to cylindrical or wafer shape in cases where they are made by casting. Fabrication by powder metallurgy allows the parts to be pressed to the approximate final desired geometry and dimensions. Electrical connections of low electrical resistance are then applied by gas pressure bonding. Gas pressure bonded contacts with either niobium, tantalum, platinum, or molybdenum applied at a pressure of 10,000 p.s.i. at 1650° C. for one hour at temperature and pressure form excellent junction contacts capable of withstanding repeated thermal cycling.

The following examples represent preferred embodiments of this invention in which zirconium is the preferred metal of the dispersed phase. It should be understood, however, that the same techniques are equally applicable to fabricating and using other thermoelectric compositions falling within the scope of our claim.

**EXAMPLE I**

A series of powdered mixtures containing varying amounts of Y_{2}O_{3}, ZrO_{2}, and zirconium were homogenously blended and consolidated into shapes by hot pressing under a pressure of 2500 p.s.i. at 1950° C. Photomicrograph of the resultant densified structure indicated a matrix consisting of Y_{2}O_{3}, ZrO_{2}, and Zr with a fairly uniform dispersion of Zr in the metal. Thermal conductivity measurements showed that the inclusion of zirconium metal in the ZrO_{2}-Y_{2}O_{3} matrix increased the thermal conductivity somewhat over yttria-stabilized zirconia without the metal. On the other hand, there was a corresponding and much larger decrease in the electrical resistivity at high temperature. Thus, for example 8 weight percent zirconium metal in the composition resulted in an increase in thermal conductivity of 15% over yttria-stabilized zirconia without Zr, coupled with a corresponding decrease in the electrical resistivity by a factor of 50 at high temperature. This resulted in an improvement in the thermoelectric figure of merit by a factor of 15 at 2000° C. over the Y_{2}O_{3}-ZrO_{2} combination without the zirconium addition.

The relative effective of yttria and zirconium on the electrical resistivity of the Y_{2}O_{3}-ZrO_{2} composition are shown in FIGS. 1 and 2. The compositions studied showed that the variation in the Y_{2}O_{3}-ZrO_{2} composition does not significantly affect the Seebeck coefficient but does noticeably change the electrical resistivity requirements. Hence, it is desirable to keep the yttria and any other oxide additive at a minimum concentration required to stabilize the zirconia. The effect of Zr on the Seebeck coefficient and the optimization parameter S^2/ρ is shown in FIGS. 3, 6, and 12, respectively.

FIG. 12 shows that the least optimization parameter is achieved with 8 weight percent zirconium with lower values shown for higher and lower amounts of zirconium. FIG. 7 shows that a 12 Y_{2}O_{3}-8 ZrO_{2}-8 Zr reaches a figure of merit (ZT=TS^2/ρK) of 0.8 at 2200° C. The relative effective of other metals within the scope of the invention in comparison to Zr and Y_{2}O_{3}-ZrO_{2} composition without a metal additive are shown in FIGS. 3 and 4. The compositions containing titanium and vanadium as additives have lower Seebeck coefficients and higher electrical resistances. Thus, while they constitute improvements over the basic ZrO_{2}-Y_{2}O_{3} composition because of lower resistivity, they are not as effective as zirconium additions. The compositions containing yttrium metal are closer to zirconium but have a higher electrical resistivity over comparable concentrations. Additions of hafnium resulted in gross deviations in Seebeck coefficients depending on whether the specimen was heated or cooled.

**EXAMPLE II**

A single cell thermoelectric generator was fabricated by ball milling a mixture of 12 Y_{2}O_{3}-8 ZrO_{2}-8 Zr powder to a particle size of less than —325 mesh (44 microns). The mixed powders were isostatically pressed at 70,000 p.s.i. and sintered in argon for 2 hours at 2400° C. The generator consisted of a cylinder (3.6 cm. outer diameter, 2.2 cm. inner diameter, 45 cm. long) slip-fitted on outside and inside diameters with 3.5 mm. thick molybdenum sleeves to serve as electrical contacts. The inside surface temperature, which served as the cold junction, was regulated by varying the flow of an inert gas through a heat exchanger in the bore. The outside surface served as the hot junction. Power testing was conducted by inductively heating the hot junction. At hot and cold junctions of 2200° C. and 1600° C., respectively, the generator produced more than 1.5 watts of electrical power.

The high temperature stability of the sintered 12 Y_{2}O_{3}-8 ZrO_{2}-8 Zr specimen was evaluated by noticing changes in electrical properties. Tests were conducted in which the Seebeck coefficient and electrical resistivity were simultaneously determined as a function of time with a 400° C. temperature gradient across the specimen at a hot junction temperature of 2000° C. or 24 hours in an argon atmosphere. The results showed that after an initial period (about 8 hours) in which the Seebeck coefficient and electrical resistivity rose slightly, the electrical properties remained constant over the remaining test period. The results were the same for sintered or fused specimens.
EXAMPLE III

A thermoelectric device was fabricated as described in Example II from a composition consisting of 93 weight percent ZrO₂ and 7 weight percent Zr. Its general configuration was cylindrical 2.2 cm. outer diameter, 1.6 cm. inner diameter and 6.5 cm. long. Slip-fitted on the outside and inside diameters were two niobium tubes to act as electrical contacts. The three components making up the thermoelectric module were pressure-bonded at 1700 kilograms/cm² and 1600° C. for one hour completely bonded the niobium to the walls of the thermoelectric material and gave a minimum electrical junction resistance. Electrical power was drawn from the thermoelectric module by heating the center of the module and cooling the outside. The module was operated at a hot junction temperature of 2000° C. and a cold junction temperature of 1500° C. for approximately 30 hours. A constant current of 15 amperes at 0.1 volt was obtained throughout the test period.

This example shows that the stabilizing oxide additive is not essential from the standpoint of thermoelectric properties. The stabilizing oxide does function, however, to impart dimensional stability to the thermoelectric composition due to phase changes, possible compound formation and in particular to the characteristic reversible monoclinic tetragonal phase change which begins to occur at about 1000° C. Minor amounts of the tetragonal phase have been noted even at 1400° C.

The effect of this phase change on the dimensional stability of the formed thermoelectric composition is shown in FIG. 5 on which heating and cooling curves are plotted as a function of temperature for thermoelectric compositions with and without yttria. The heating and cooling curve for the specimen without the oxide additive clearly shows a decrease hysteresis effect due to the expansion and contraction of zirconia as it passes from one crystallographic change to another over that for pure zirconia. The advantage of using a phase-stabilizing concentration of the selected oxides is thus apparent from FIG. 5. In the case of yttria, the monoclinic phase will disappear when as little as 6 or 7 percent is incorporated in the initial powder blend. As increasing amounts, up to 15 percent, are used the zirconia will have completely been stabilized in the cubic habit. The same general effect will be noted in the other members of the class of stabilizing oxides herein discussed.

It will be seen that there has been described a class of zirconia-based thermoelectric compositions capable of generating electrical power at temperatures of the order of 2000° C. The basic thermoelectric components consist of a matrix of zirconia and a metal selected from zirconium, titanium, vanadium, and yttrium, and a fairly homogeneous dispersion of the selected metal as a dispersed phase. In order to render such an element dimensionally stable against crystalline changes as the element undergoes heating and cooling cycles a metal oxide selected from yttria, calcia, and a 4/7 rare earth oxide is added to stabilize the ZrO₂ into a single crystalline habit.

In the specification and claim the thermoelectric element is described in terms of its initial components. Thus, while the thermoelectric element is described in terms of zirconia, ZrO₂, the final composition of the fabricated element has probably resulted in conversion of ZrO₂ into different chemical forms by combination with the other components of the starting mixture.

All concentrations of metal and oxide are to be read in terms of weight percent of the total composition.

What is claimed is:
1. A thermoelectric element comprising a densified body having electrical leads at opposed portions of said body, said body formed by a process of intimately mixing zirconia, a metal selected from zirconium, titanium, vanadium, and yttrium, and a metal oxide selected from yttria, calcia, and a 4/7 rare earth metal oxide, and densifying the resultant mixture by heating said mixture to at least its sintering temperature in an inert atmosphere and at a pressure sufficient to form a dense coherent body having a matrix of zirconia and said metal oxide in which the concentration of said metal is between about 4 weight percent and its solubility limit in said matrix at the intended service temperature.

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