Oct. 29, 1957 R. W. FRITTS ET AL 2,811,441

ELECTRICALLY CONDUCTIVE COMPOSITION AND METHOD OF MANUFACTURE THEREOF

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Fig. 1.

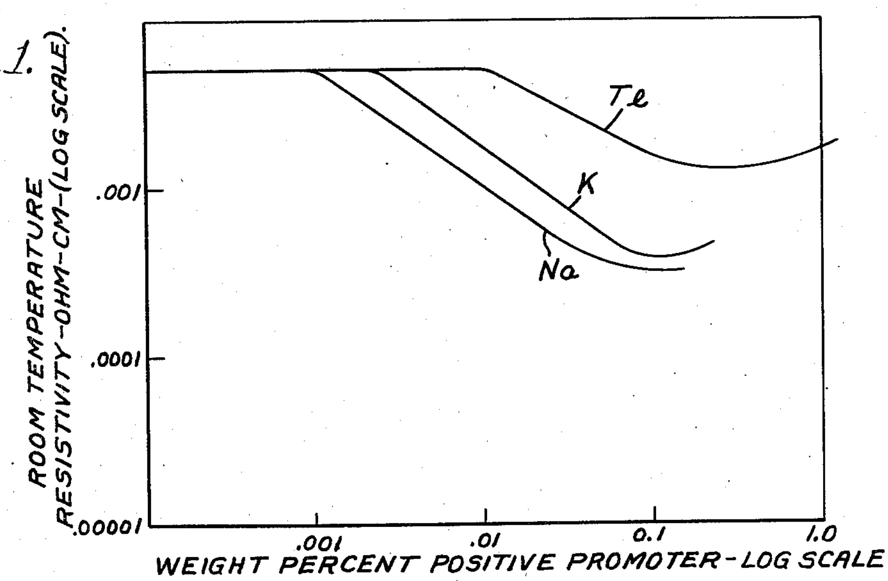
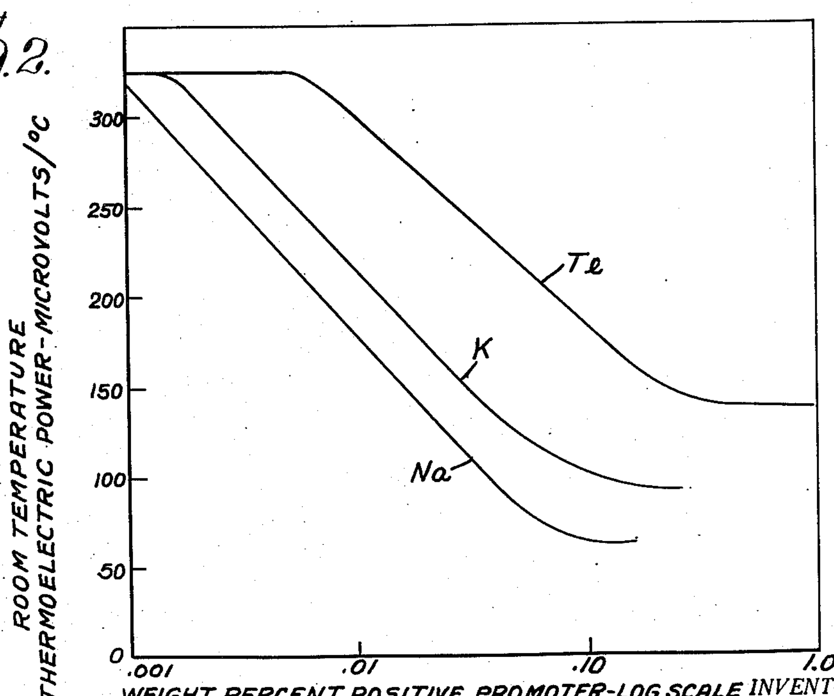


Fig. 2.



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ELECTRICALLY CONDUCTIVE COMPOSITION AND METHOD OF MANUFACTURE THEREOF

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9 Claims. (Cl. 75—166)

This invention relates to semi-metallic alloys or compositions, composed in the main of lead and tellurium, and more particularly, to electrical conductors comprising such alloys or compositions.

It is an object of the invention to provide electrically conductive alloys or compositions as aforesaid having new relationships of certain electrical characteristics.

A further object is to provide electrically conductive alloys or compositions of the character indicated, in which the magnitudes of certain of the electrical characteristics thereof are reproducible within desired ranges therefor.

Another object is to provide electrically conductive alloys or compositions of the character indicated, the resistivity of which may be controlled in magnitude as desired.

A further object of the invention is to provide electrically conductive alloys or compositions as aforementioned, in which desired resistivities therefor are reproducible.

Another object is to provide electrically conductive alloys or compositions of the character indicated, the thermo-electric power of which may be controlled in magnitude as desired.

A further object is to provide electrically conductive alloys or compositions as aforementioned, having new relationships of thermoelectric power and resistivity, and which are readily reproducible within desired ranges of such relationships.

A further object of the invention concerns a method of fabrication of the aforementioned alloys or compositions to provide for the reproducible production thereof within desired ranges of thermoelectric power and resistivity.

A further object is to provide alloys or compositions as aforementioned having adequate mechanical strength for practical applications.

A further object is to provide electrically conductive alloys or compositions of the character abovementioned which are chemically stable over a temperature range up to 400° C. when shielded from oxidizing atmosphere.

A further object is to provide electrical conductors composed of the alloys or compositions of the present invention.

Now, in order to acquaint those skilled in the art with the manner of practicing and utilizing the present invention, there is hereinafter disclosed certain preferred embodiments of the invention.

In the drawings:

Figure 1 is a graphic illustration of the resistivity characteristics of the electrically conductive semi-metallic alloys or compositions of the invention, within certain ranges of additions of positive promoters therein: and

Figure 2 is a graphic illustration of the thermo-electric power characteristics of the electrically conductive semi-metallic alloys or compositions depicted in Figure 1.

The invention described and claimed herein utilizes a lead-tellurium base composition or alloy consisting essentially of lead in the range of 59.0% to 61.8% by weight, balance substantially all tellurium, and which base composition contains not more than 0.001% by weight of other matter.

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Lead-tellurium base alloys within the aforementioned range and of the aforementioned purity are positive electrical conductors and exhibit high positive thermoelectric power, nominally higher electrical resistivity, and low thermal conductivity with respect to a metal. Such compositions or alloys have utility as electrical conductors.

In lead-tellurium base alloys of the aforementioned range and purity, the magnitudes of the thermoelectric power and electrical resistivity of the aforementioned base lead-tellurium alloys can be varied only through a limited range, since such characteristics are, we have found, strongly dependent upon the equilibrium temperature from which they are cooled during fabrication.

The aforementioned lead-tellurium alloys may be best described metallographically as a two-phase alloy. It has been observed that these alloys, when sectioned and examined microscopically, comprise a major phase comprising crystal grains varying usually from 1 to 10 millimeters in size and between such grains there exist thin relatively lighter regions of a second phase. The grains of the primary phase are crystals of the intermetallic compound lead-telluride which contain approximately 61.88% lead by weight. The lighter second phase, clearly discernible at the grain boundaries, is tellurium containing a minor concentration of lead.

The function of the second phase in such alloys is thought to be threefold. First, the thermal equilibrium between the two phases, which is established by the heat treatment aforementioned, induces positive thermoelectric power and conductivity in the primary lead-telluride phase which, because of its high concentration in the alloy, controls the electrical properties of the two-phase alloy. Secondly, the thin layers act as a cementing agent for the grains of the primary phase, thereby improving the mechanical strength of the alloy when compared to that of the pure intermetallic compound. This cementing action of the second phase improves the strength of an alloy in tension and compression at all temperatures up to 400° C. Thirdly, the second phase affords good electrical continuity in the polycrystalline alloy by rendering the intergranular component of electrical resistivity negligible. We have found that the actual concentration of second phase is not critical so long as the composition is maintained within the aforementioned specified ranges.

Lead-tellurium alloys containing less than 38.2% tellurium by weight do not usually exhibit reproducible physical and electrical properties when in a polycrystalline state, and in alloys containing more than 41.0% tellurium by weight the second phase regions are of such dimension that the electrical conductivity along the grain boundaries of the alloy cannot be neglected when compared with the conductivity through the primary phase. Moreover, unless the specified purity is adhered to, third element "promoters" hereinafter described will not afford reproducibility of electrical characteristics in the resultant alloy. Accordingly, the specified composition ranges and purity are to be considered critical.

It will be observed that since the lead-tellurium base alloys must be slowly cooled from the annealing temperature to afford adequate strength, little variation in the electrical properties can be afforded by altering the temperature of the anneal. Accordingly, for applications requiring greater variations of such values of electrical characteristics arbitrary changes in these characteristics must be derived from the adjustment of factors other than temperature and annealing history.

We have discovered that the electrical characteristics of lead-tellurium base alloys or compositions of the aforementioned range and purity can be markedly and advantageously altered in a reproducible manner by the addition thereto of controlled amounts of matter other than lead or tellurium. For convenience, these additions are herein designated "third element additions" to distinguish them from the lead and tellurium constituents of the alloys of the invention.

The "third element additions" which we have found effective, for the purposes of the present invention when added in minor amounts to the lead-tellurium base alloy aforementioned are: sodium, potassium, and thallium.

The third element additions aforementioned are "positive promoters" in the sense that the positive polarity of the base alloy aforementioned remains unchanged with additions of the "third element promoters" aforeindicated. For the purposes of this specification and claims a "positive" composition or alloy and a "positive" conductor is to be understood as meaning an alloy composition or conductor which exhibits positive conductivity as evidenced by Hall effect measurements or thermoelectric effect measurements both taken at room temperature.

As best illustrated in Figures 1 and 2 increasing concentrations of the third element addition or positive promoter cause increases in the conductivity with relatively slight decrease in the thermoelectric power of the resulting alloy, as compared to that of the lead-tellurium base alloy, while the positive polarity of the conductivity and thermoelectric power of the base alloy is maintained.

Table I below, first column thereof, lists certain elements which we have found effective as positive promoters when added to the aforementioned lead-tellurium base alloys or compositions. Second column of Table I lists the order of the maximum concentration limits by weight percent of such promoters to the base alloy effective for achieving the objects of the invention. It is to be understood that these concentration limits are the maximum which effectively alter the electrical properties of the base alloy. Concentrations in excess of the stated amounts of such additives have no appreciable effect in beneficially altering the electrical properties with which this invention is concerned, and in this sense the limits indicated are to be considered critical. The third and fourth columns of Table I set forth the electrical properties at room temperature of lead-tellurium alloys promoted with the maximum useful concentrations of the positive promoters, after high temperature annealing as hereinafter disclosed.

Table I

Positive Promoters	Order of Maximum Effective Concentration Limits by Weight Percent	Thermoelectric Power, Microvolts/° C.	Resistivity, Ohm-Cm.
Sodium	0.14	+65	0.00033
Potassium	0.23	+90	0.00037
Thallium	0.60	+138	0.0013

Figures 1 and 2 of the drawings may be here referred to for a graphic illustration of the effect of the additions of the positive promoters of Table I with respect to the resistivity and thermoelectric power characteristics (measured at room temperature) afforded by addition to the lead-tellurium base alloys or compositions of each of the positive promoters set forth in Table I, and with the variations indicated in the amount thereof added in each case.

As aforementioned, the lead-tellurium base alloy previously described, is a two-phase alloy. When the aforedescribed third element additions are incorporated in the base alloy, such third element additions become distributed between the two phases. We have discovered that the nature of such distribution has negligible effect upon the electrical properties of the composition.

In Table I above, the thermoelectric power and resistivity data given is for the 61.7% lead, balance substantially all tellurium composition containing the third element addition in question in the amount indicated in the table. Such data, for the amount of promoters present will remain substantially the same for any base composition within aforementioned range.

In connection with the aforementioned Figures 1 and 2, the logarithm of the percent by weight concentration, and the logarithm of the resistivity have been plotted for convenience, as will be understood by those skilled in the art, while thermoelectric power has been plotted linearly.

It will be observed upon examination of the data recorded in Figures 1 and 2, that a wide range of electrical properties can be induced in lead-tellurium base alloys by third element addition. Sodium additions, for example, can reduce the resistivity of the lead-tellurium base alloy by a factor of approximately 15, while reducing the thermoelectric power by a factor of 5.

The aforedescribed alloys or compositions and electrical conductors comprising the invention may be fabricated by melting together the alloy constituents aforementioned, within the concentration limits aforeindicated. It is to be understood, however, that, as has been previously indicated, the lead-tellurium alloys of the invention must be of a high order purity, i. e., containing not in excess of the order of 0.001% by weight impurity. Such purity has been found to be necessary in practicing the present invention if the electrical properties of the alloys of this invention are to be reproducible. It is to be understood, however, that selenium, because of its chemical similarity to and natural occurrence with tellurium, is frequently a contaminant in commercial tellurium, and is difficult and expensive to remove to the extent of purity as specified above. We have found, however, that selenium concentrations of the order usually found in commercially pure tellurium, usually of the order of 1%, cause no significant changes in the electrical properties of the alloys of this invention.

In the production of the new alloys or compositions of our invention and electrical conductors comprising the same, the constituents are melted at from 920° C. to 1100° C. under a reducing atmosphere, and agitated to insure uniform distribution. The alloy may then be cast, formed or machined as desired. It is then preferably annealed to insure normalization of the alloy or composition. Such annealing may be accomplished at temperatures ranging from 540° C. to 815° C. for from 10 to 20 hours, the lesser time being required at the higher temperature. The aforementioned annealing may be conveniently accomplished by sealing the ingots of the alloy or composition within a quartz or Vycor envelope under a hydrogen atmosphere. This prevents loss of material and hence preservation of the ingots during annealing and affords a simple method of handling. After heating, the sealed tube is slowly cooled to room temperature, i. e., at a rate of 50° C. per hour or less. A higher rate of cooling may reduce the physical strength of the ingot.

The third element promoted alloy or composition aforedescribed is a two-phase alloy having improved electrical properties as compared to the corresponding properties of the lead-tellurium base alloy. For example, with additions of third element promoters as aforedescribed the resistivity of such base alloys can be reduced significantly with but little relative reduction in thermoelectric power. Moreover, addition of such third element promoters affords the alloys a much greater range of relationships and magnitudes of the electrical characteristics than are found in the lead-tellurium base alloy, thereby markedly increasing their utility for practical applications.

Compositions of the present invention exhibit the desired physical properties aforementioned. More specifically, they are mechanically strong and stable under operating conditions. The coefficient of thermal expansion is of the order of $18\times10^{-6}/°$ C.

We claim:

1. An alloy containing as two of its essential constituents lead and tellurium, the percent by weight of lead being 59.0% to 61.8%, balance substantially all tellurium, and the alloy containing no more than 0.001% by weight other matter except for limited effective amounts of a promoter from the group consisting of sodium, potassium and thallium affording the alloy reproducible variation of and control over the electrical properties thereof.

2. A lead1tellurium composition containing from 59.0% to 61.8% by weight lead, and the balance substantially all tellurium, and at least one member selected from the group consisting of, sodium, potassium, and thallium, in an effective amount not in excess by weight percent of the lead and tellurium of said members as follows: 0.14 sodium; 0.23 potassium; and 0.60 thallium.

3. A composition consisting essentially of lead and tellurium containing 59.0% to 61.8% lead by weight, balance substantially all tellurium, and containing a promoter selected from the group consisting of sodium, potassium, and thallium and containing not more than 0.001% by weight of other matter.

4. A positive electrical conductor consisting essentially of lead and tellurium containing 59.0% to 61.8% lead by weight, balance substantially all tellurium, and containing not more than 0.001% by weight of other matter, except for, sodium, potassium, and thallium in an effective amount by weight percent thereof of the lead-tellurium not more than 0.14 sodium; 0.23 potassium; and 0.60 thallium, respectively.

5. A lead-tellurium composition, consisting essentially of from 59.0% to 61.8% by weight lead, and the balance substantially all tellurium, and sodium in an effective amount not in excess of 0.14% by weight of the lead and tellurium.

6. A lead-tellurium composition, consisting essentially of from 59.0% to 61.8% by weight lead, and the balance substantially all tellurium, and potassium in an effective amount not in excess of 0.23% by weight of the lead and tellurium.

7. A lead-tellurium composition, consisting essentially of from 59.0% to 61.8% by weight lead, and the balance substantially all tellurium, and thallium in an effective amount not in excess of 0.60% by weight of the lead and tellurium.

8. The method of controlling the electrical characteristics of a lead-tellurium composition consisting essentially of from 59.0% to 61.8% lead by weight, and the balance substantially all tellurium, which comprises alloying therewith at least one member selected from the group consisting of sodium, potassium, and thallium, in an effective amount not in excess by weight percent of the lead and tellurium of said members as follows: 0.14 sodium; 0.23 potassium; and 0.60 thallium, respectively.

9. The method of controlling the electrical characteristics of a lead-tellurium composition consisting essentially of from 59.0% to 61.8% lead by weight, and the balance substantially all tellurium, which comprises alloying therewith at least one member selected from the group consisting of sodium, potassium, and thallium, in an effective amount not in excess by weight percent of the lead and tellurium of said members as follows: 0.14 sodium; 0.23 potassium; and 0.60 thallium, respectively, and then annealing the resultant composition at a temperature of from about 540° C. to 815° C.

No references cited.