Oct. 29, 1957 R. W. FRITTS ET AL **2,811,440**

ELECTRICALLY CONDUCTIVE COMPOSITIONS
AND METHOD OF MANUFACTURE THEREOF

Filed Dec. 15, 1954 4 Sheets-Sheet 1

Fig. 1.

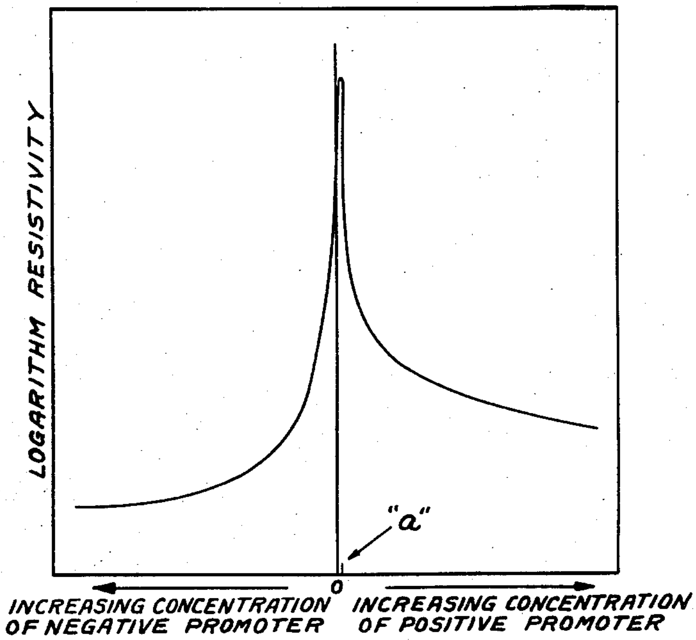
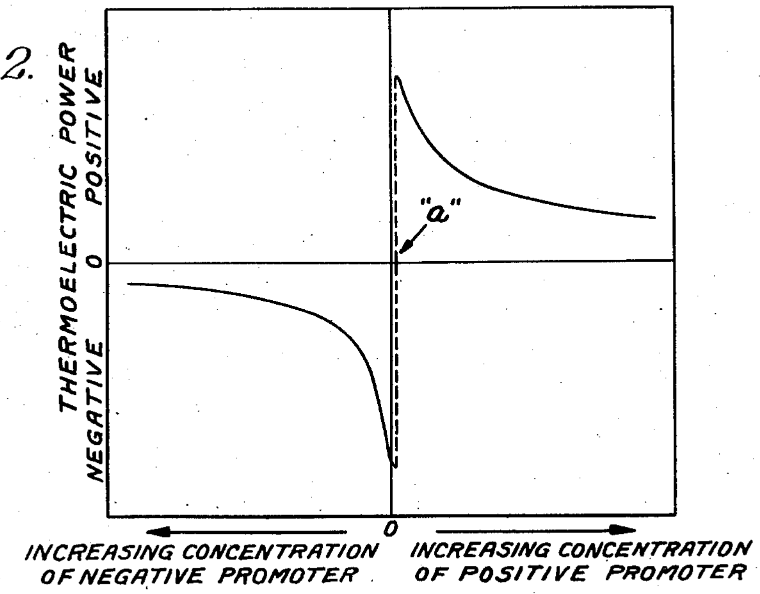


Fig. 2.



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Filed Dec. 15, 1954 4 Sheets-Sheet 2

Fig. 3.

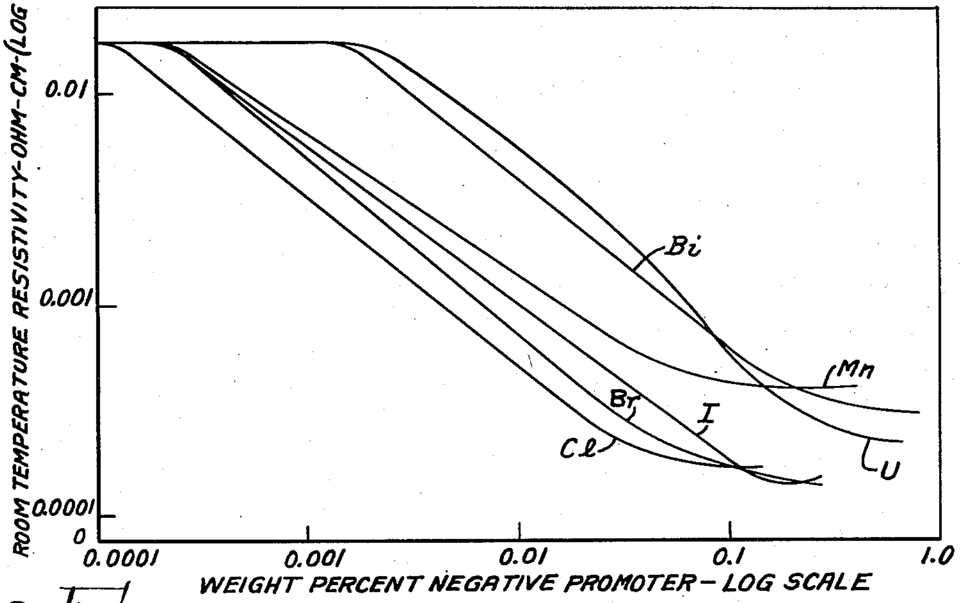

Fig. 3A.

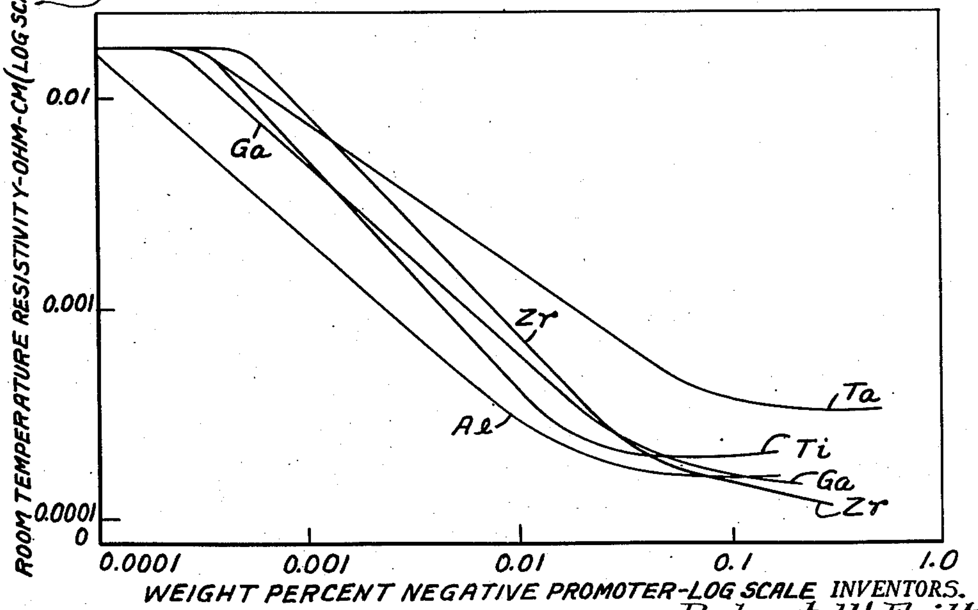

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Fig. 4.

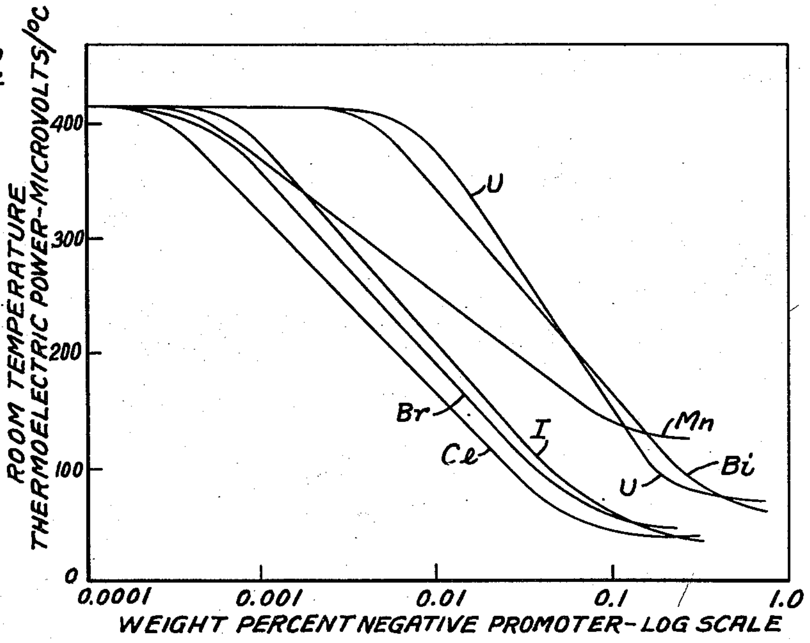
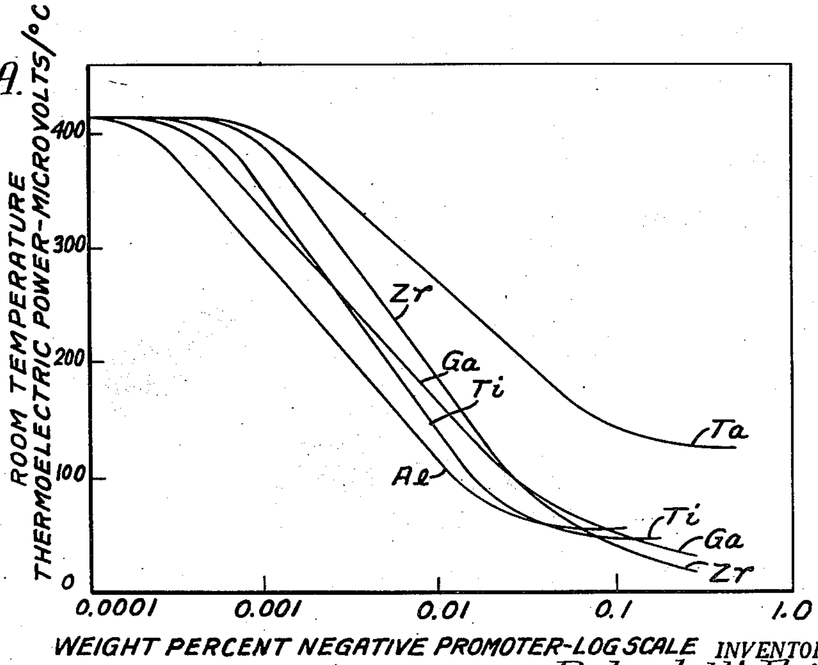


Fig. 4A.



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ELECTRICALLY CONDUCTIVE COMPOSITIONS
AND METHOD OF MANUFACTURE THEREOF

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Fig. 5.

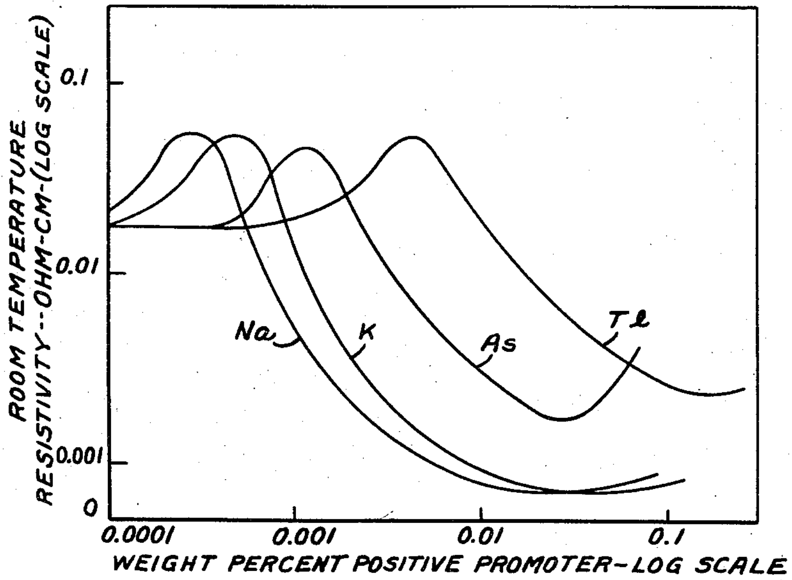
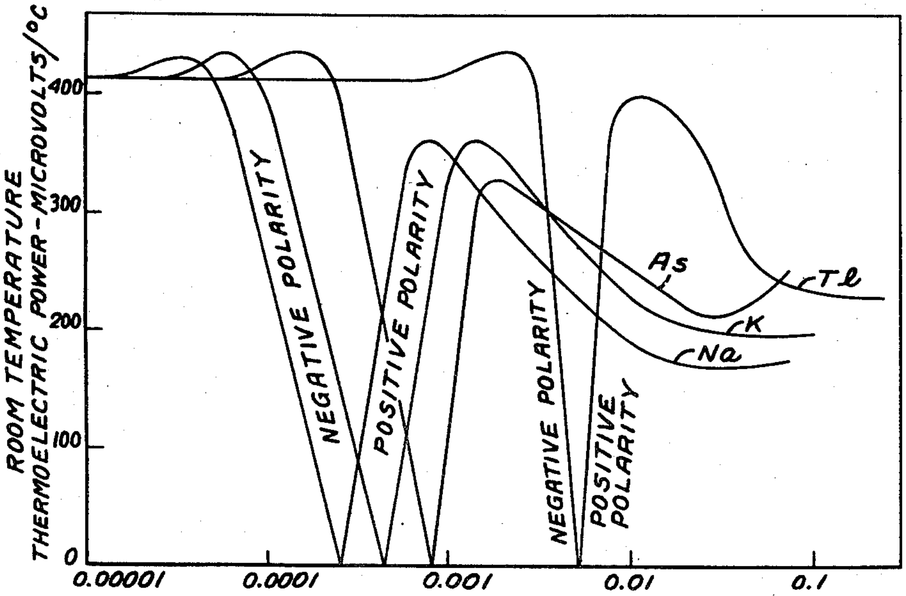


Fig. 6.



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ELECTRICALLY CONDUCTIVE COMPOSITIONS AND METHOD OF MANUFACTURE THEREOF

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Application December 15, 1954, Serial No. 475,541
20 Claims. (Cl. 75—166)

The present application is a continuation-in-part of our copending application, Serial No. 442,844, filed July 12, 1954, now abandoned.

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.

A further object is to provide electrically conductive alloys or compositions of the character indicated, the electrical conductivity of which may be either positive or negative, as desired.

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 is to provide electrically conductive alloys or compositions as aforementioned, the electrical characteristics, particularly with respect to polarity, of which are controllable and reproducible.

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 thermoelectric power of which may be controlled in magnitude as desired.

A further object is to provide electrically conductive alloys or compositions as aforementioned in which the polarity of thermoelectric power may be either positive or negative 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 is to provide electrically conductive alloys or compositions, the electrical characteristics of which are substantially independent of prior heat treatment.

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 a method as last mentioned for arbitrarily rendering such alloys or compositions either of positive or negative polarity.

A further object is to provide alloys or compositions as

aforementioned having adequate mechanical strength for practical applications over a wide temperature range.

A further object is to provide electrically conductive alloys or compositions of the character abovementioned which are chemically stable over a wide temperature range 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 generally indicating the effect of various concentrations of negative and positive promoters with respect to the resistivity characteristics of the electrically conductive semi-metallic alloys or compositions of the invention;

Figure 2 is a graphic illustration generally indicating the effect of various concentrations of negative and positive promoters with respect to the thermoelectric power characteristics of the electrically conductive semi-metallic alloys or compositions of the invention;

Figures 3 and 3A are graphic illustrations of the resistivity characteristics of certain of the electrically conductive semi-metallic alloys or compositions of the invention, within certain ranges of additions of negative promoters therein;

Figures 4 and 4A are graphic allustrations of the thermoelectric power characteristics of the electrically conductive semi-metallic alloys or compositions depicted in Figures 3 and 3A, respectively.

Figures 5 is a graphic illustration of the resistivity characteristics of certain of the electrically conductive semi-metallic alloys or compositions of the invention, within certain ranges of additions of positive promoters therein; and

Figure 6 is a graphic illustration of the thermoelectric power characteristics of the electrically conductive semi-metallic alloys or compositions depicted in Figure 5.

The invention described and claimed herein utilizes a lead-tellurium base composition or alloy consisting essentially of lead in the range of 61.95% to 63.0% by weight, balance substantially all tellurium, and which base composition contains not more than 0.001% by weight of other matter.

Lead-tellurium base alloys within the aforementioned range and of the aforementioned purity are negative electrical conductors and exhibit high negative 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 are, we have found, strongly dependent upon the heat treatment afforded the alloy during fabrication, thereby affording control over such properties by the heat treatment.

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 darker regions of a second phase. The grains of the primary phase are crystals of the intermetallic compound lead-telluride which contain approximately 61.89% lead by weight. The darker second phase, clearly discernible at the grain boundaries, is lead containing a minor concentration of tellurium.

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 negative 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 815° 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 61.95% lead by weight do not usually exhibit reproducible physical and electrical properties when in a polycrystalline state, and in alloys containing more than 63.0% lead 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 ranges of compositions and purity are adhered to, third element "promoters" hereinafter described will be rendered ineffective. Additionally, alloys having large concentrations of the aforementioned second phase are subject to plastic flow at high temperatures and for this further reason are not desirable for high temperature applications. Accordingly, the specified composition ranges and purity are to be considered critical.

It will be observed that since the electrical properties of the aforementioned alloys or compositions are dependent upon the equilibrium temperature from which they have been quenched, use of such alloys or compositions is limited to such temperatures as will not affect the electrical characteristics established by the quenching treatment. Accordingly, for high temperature applications requiring fixed 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 further 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: Bismuth, tantalum, manganese, zirconium, titanium, aluminum, gallium, chlorine, bromine, iodine, uranium, sodium, potassium, thallium, and arsenic.

The third element additions aforementioned may be either "positive promoters" or "negative promoters" as hereinafter defined, and the resultant alloy or composition may be a "positive" or "negative" alloy or composition or conductor, as also hereinafter defined.

A "negative" composition or alloy and a "negative" conductor is to be understood through this specification as meaning an alloy, composition or conductor which exhibits negative conductivity as evidenced by Hall effect measurements or thermoelectric effect measurements, both taken at room temperature. Similarly, 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.

"Negative promoters" are those which, when added to the lead-tellurium base alloy previously defined, alter the electrical conductivity without changing the polarity of the conductivity or thermoelectric power of the base alloy (it being negative according to the preceding definition). "Positive promoters" are those which, when added to the lead-tellurium base alloy, cause at first, with very small additions, reduction in the conductivity of the alloy to a minimum value beyond which further increase in the concentration of the positive promoter causes an increase in the conductivity of the alloy accompanied by a reversal in the polarity of the conductivity and thermoelectric power, i. e., from negative to positive.

The functions of such negative and positive promoters should be contrasted for sake of clarity as follows:

(1) Increasing concentrations of the negative promoter elements cause increases in the conductivity and decrease of the thermoelectric power of the resulting alloy, as compared to that of the lead-tellurium base alloy, while preserving the negative polarity of the conductivity and thermoelectric power thereof.

(2) Increasing concentrations of positive promoter elements cause initially reductions in the conductivity and increase in the thermoelectric power of the lead-tellurium base alloy, until a minimum conductivity is reached whereupon the thermoelectric power and conductivity reverse polarity to the positive sense, and further increase in the concentrations of the positive promoter causes increase in the conductivity and decrease of the thermoelectric power in the resulting alloy.

The aforeindicated effects are graphically illustrated in Figures 1 and 2, wherein the effect of varying the concentrations of the aforementioned negative and positive promoters are plotted. In both Figures 1 and 2, the central vertical axes give the properties of the aforedescribed base lead-tellurium alloy or composition. The left halves of each of the figures characterize the change, at room temperature, of the electrical properties of the lead-tellurium base alloys or compositions with the addition of the aforementioned negative promoters. It will be observed that the two drawings, Figures 1 and 2, have no scale applied thereto since the concentration ranges differ for each of the third element additions to be hereinafter described due to variations in atomic weights and concentration limits. The right halves of each of Figures 1 and 2 show the changes in the electrical properties as positive promoters are added to the base alloy or composition. It should be noted that for a given promoter element the maximum resistivity and the polarity reversal of the thermoelectric power occur at the same concentration. This concentration is indicated by "*a*" in Figures 1 and 2.

Table I below, first column thereof, lists certain elements which we have found effective as negative 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 negative promoters, after high temperature annealing as hereinafter disclosed.

Table I

Negative Promoters	Order of Maximum Effective Concentration Limits by Weight Percent	Thermoelectric Power, Microvolts/° C.	Resistivity, Ohm-Cm.
Bismuth	[1] 0.60–1.20	−72	0.00031
Tantalum	0.50	−121	0.00032
Manganese	0.25	−113	0.00036
Zirconium	0.25	−23	0.00012
Titanium	0.15	−45	0.00020
Aluminum	0.10	−59	0.00016
Gallium	0.25	−36	0.00015
Chlorine	0.10	−45	0.00019
Bromine	0.20	−47	0.00015
Iodine	0.25	−45	0.00015
Uranium	0.80	−72	0.00020

[1] The range set forth is discussed below.

Figures 3, 3A, 4 and 4A of the drawings may be here referred to for a graphic illustration of the effect of the additions of the negative 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 negative promoters set forth in Table I, and with the variations indicated in the amount thereof added in each case.

As previously mentioned, certain positive promoters may also be alloyed with the aforementioned lead-tellurium alloys, and such promoters are listed in column 1 of Table II below. The second column of Table II, like the corresponding column of Table I, sets forth 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. Again, it will be observed that concentrations of the positive promoters to the lead-tellurium base alloy in amounts in excess of that contained in column 2 of Table II 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.

Column 3 of Table II sets forth the concentration by weight percent of the positive promoters listed at which the polarity of conductivity and thermoelectric power of the promoted alloy reverses. These are the concentration values for the promoters respectively, indicated generally by point "*a*" in Figures 1 and 2.

Columns 4 and 5 set forth the thermoelectric power and resistivity characteristics at room temperature of the alloy or composition resulting from the addition of the aforedescribed positive promoters in the amount shown in column 2 after high temperature annealing and subsequent slow cooling as hereinafter disclosed.

Table II

Positive Promoters	Order of Maximum Effective Concentration Limit By Weight Percent	Concentration, Weight percent at which Polarity Reverses (Point "*a*" Figures 1 and 2)	Thermoelectric Power, Microvolts/° C.	Resisitivity, Ohm-Cm.
Sodium	0.06	.0002	+173	0.00074
Potassium	0.10	.0004	+198	0.00076
Thallium	[1] 0.25–1.00	[1] .005 to .02	+256	0.00290
Arsenic	[1] 0.07–0.25	[1] .0008 to .002	+270	0.00450

[1] The range set forth is discussed below.

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 all cases except that of bismuth, thallium and arsenic. Accordingly, in the case of bismuth, thallium and arsenic, the maximum

effective concentration is dependent upon the lead content of the lead-tellurium base alloy within the ranges stated therefor in Tables I and II. We have found 1.20% by weight bismuth to be the maximum effective concentration for lead-tellurium base alloys containing 63.0% lead; for base alloys containing less lead the maximum effective bismuth concentration is somewhat less, that is ranges down to 0.60% by weight when the lead content ranges down to 61.95%. Similarly, in the case of thallium, the maximum effective concentration is dependent upon the lead content of the lead-tellurium base alloy within the range stated therefor. We have found 1.00% by weight thallium to be the maximum effective concentration for lead-tellurium base alloys containing 63.0% lead; for base alloys containing less lead, the maximum effective thallium concentration is somewhat less, that is ranges down to .25% by weight when the lead content ranges down to 61.95%. Similarly, in the case of arsenic, the maximum effective concentration is dependent upon the lead content of the lead-tellurium base alloy within the range stated therefor, and ranges from 0.25% for base alloys containing 63.0% lead down to 0.07% for base alloys containing 61.95% lead. As indicated in Table II, the concentration weight percent at which the polarity reverses in the case of thallium promoted base alloy ranges from .005 to .02 as the lead constituent of the lead-tellurium base composition varies from 61.95% to 63.0%. Similarly, in the case of the arsenic promoted base alloy the concentration weight percent at which polarity reverses ranges from .0008 to .002 as the lead content of the base alloy varies from 61.95% to 63.0%. This behaviour of bismuth, thallium and arsenic is thought to be due to the formation of a bismuth-lead-tellurium, a thallium-lead-tellurium or an arsenic-lead-tellurium complex within the intergranular phase aforementioned which accounts for a portion of the addition. All other third element additions aforementioned, both positive and negative, form complexes with the second or intergranular phase aforementioned to a much lesser extent than do bismuth, thallium and arsenic and for purposes of this invention, in the cases of such other additions these effects are inconsequential. Accordingly, no change in the concentration limits thereof are necessary as the proportions of lead and tellurium in the base alloy vary within the range stated therefor.

In Tables I and II above, the thermoelectric power and resistivity data given is in both cases for the 61.95% lead, balance substantially all tellurium composition containing the third element addition in question in the amount indicated in the Table (in the case of bismuth, thallium and arsenic, the lower maximum effective amount indicated).

Figures 5 and 6 of the drawings may be here referred to for a graphic illustration of the effect of the additions of the positive promoters of Table II 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 II, and with the variations indicated in the amount thereof added in each case.

In connection with the aforementioned Figures 3 to 6, 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 through 6, that a wide range of electrical properties can be induced in lead-tellurium base alloys by third element additions, either positive or negative as desired. Zirconium additions, for example, can reduce the resistivity of the lead-tellurium base alloy by more than a factor of approximately 100, while reducing the thermoelectric power by a factor of 20.

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 of 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 may be slowly cooled to room temperature or quenched directly or at any intermediate temperature in cold water without substantially affecting the reproducibility of the desired electrical characteristics, especially as the concentration of the third element addition approaches its maximum effective concentration limit aforeindicated. Thus, the heat treatment history of the alloy or composition becomes of lesser importance in the third element addition promoted compositions aforedescribed as the concentration of the third element addition approaches the maximum effective limit aforeindicated.

The third element promoted alloy or composition is a two-phase alloy having improved electrical properties as compared to the corresponding properties of the lead-tellurium base alloy. For example, the electrical properties of the third element addition promoted alloys or compositions are governed to a lesser extent by the heat treatment given the alloy, with variations in electrical properties considerably less than the variations exhibited by the lead-tellurium base alloy to which no third element has been added. Thus, the third element additions, in effect, reduce the dependency of the electrical properties upon prior heat treatment and in this sense tend to stabilize these properties to a higher degree than that achieved in the lead-tellurium base alloy. It may be stated as a general observation that the degree of stabilization increases with the concentration of the aforementioned third element additions up to the maximum effective amount thereof as above set forth. This lesser dependency of third element addition promoted alloys or compositions aforedescribed and of electrical conductors comprising the same, markedly increases the utility thereof for high temperature applications. In this connection, however, where alloys including positive promoters are concerned and where the application temperature approaches 570° C. concentrations of the positive promoter approaching the maximum effective limit aforementioned should be used to insure maintenance of positive polarity of the composition.

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. A composition consisting essentially of a lead-tellurium base constituent consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium, and a member selected from the group consisting of, bismuth, tantalum, manganese, zirconium, titanium, aluminum, gallium, chlorine, bromine, iodine, uranium, sodium, potassium, thallium and arsenic, in an amount effective to modify the conductivity of said base constituent not in excess by weight percent of the lead and tellurium of said members as follows: 0.50 tantalum; 0.25 manganese; 0.25 zirconium; 0.15 titanium; 0.10 aluminum; 0.25 gallium, 0.10 chlorine; 0.20 bromine; 0.25 iodine; 0.80 uranium; 0.06 sodium; and 0.10 potassium; and bismuth, thallium and arsenic not in excess of from 0.60 to 1.20, from 0.25 to 1.00 and from 0.07 to 0.25, respectively, over the aforementioned range of lead.

2. A composition consisting essentially of a lead-tellurium base constituent, consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium, and bismuth in an amount effective to modify the conductivity of said base constituent not in excess of from 0.60 to 1.20 by weight of the lead and tellurium over the aforementioned range of lead.

3. A composition consisting essentially of a lead-tellurium base constituent, consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium, and tantalum in an amount effective to modify the conductivity of said base constituent not in excess of 0.50% by weight of the lead and tellurium.

4. A composition consisting essentially of a lead-tellurium base constituent, consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium, and manganese in an amount effective to modify the conductivity of said base constituent not in excess of 0.25% by weight of the lead and tellurium.

5. A composition consisting essentially of a lead-tellurium base constituent, consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium, and zirconium in an amount effective to modify the conductivity of said base constituent not in excess of 0.25% by weight of the lead and tellurium.

6. A composition consisting essentially of a lead-tellurium base constituent, consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium, and titanium in an amount effective to modify the conductivity of said base constituent not in excess of 0.15% by weight of the lead and tellurium.

7. A composition consisting essentially of a lead-tellurium base constituent, consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium, and alluminum in an amount effective to modify the conductivity of said base constituent not in excess of 0.10% by weight of the load and tellurium.

8. A composition consisting essentially of a lead-tellurium base constituent, consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium, and gallium in an amount effective to modify the conductivity of said base constituent not in excess of 0.25% by weight of the lead and tellurium.

9. A composition consisting essentially of a lead-tellurium base constituent, consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium, and chlorine in an amount effec-

tive to modify the conductivity of said base constituent not in excess of 0.10% by weight of the lead and tellurium.

10. A composition consisting essentially of a lead-tellurium base constituent, consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium and bromine in an amount effective to modify the conductivity of said base constituent not in excess of 0.20% by weight of the lead and tellurium.

11. A composition consisting essentially of a lead-tellurium base constituent, consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium, and iodine in an amount effective to modify the conductivity of said base constituent not in excess of 0.25% by weight of the lead and tellurium.

12. A composition consisting essentially of a lead-tellurium base constituent, consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium, and uranium in an amount effective to modify the conductivity of said base constituent not in excess of 0.80% by weight of the lead and tellurium.

13. A composition consisting essentially of a lead-tellurium base constituent, consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium, and sodium in an amount effective to modify the conductivity of said base constituent not in excess of 0.06% by weight of the lead and tellurium.

14. A composition consisting essentially of a lead-tellurium base constituent, consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium, and potassium in an amount effective to modify the conductivity of said base constituent not in excess of 0.10% by weight of the lead and tellurium.

15. A composition consisting essentially of a lead-tellurium base constituent, consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium, and thallium in an amount effective to modify the conductivity of said base constituent not in excess of from 0.25% to 1.00% by weight of the lead and tellurium over the aforementioned range of lead.

16. A composition consisting essentially of a lead-tellurium base constituent, consisting essentially of from 61.95% to 63.0% by weight lead, and the balance substantially all tellurium, and arsenic in an amount effective to modify the conductivity of said base constituent not in excess of from 0.07% to 0.25% by weight of the lead and tellurium over the aforementioned range of lead.

17. The method of controlling the electrical characteristics of a lead-tellurium composition consisting essentially of from 61.95% to 63.0% lead by weight, and the balance substantially all tellurium, which comprises alloying therewith at least one member selected from the group consisting of bismuth, tantalum, manganese, zirconium, titanium, aluminum, gallium, chlorine, bromine, iodine, uranium, sodium, potassium, thallium and arsenic, in an effective amount not in excess by weight percent of the lead and tellurium of said members as follows: 0.50 tantalum; 0.25 manganese; 0.25 zirconium; 0.15 titanium; 0.10 aluminum; 0.25 gallium; 0.10 chlorine; 0.20 bromine; 0.25 iodine; 0.80 uranium; 0.06 sodium; and 0.10 potassium; and bismuth, thallium and arsenic not in excess of from 0.60 to 1.20, from 0.25 to 1.00 and from 0.07 to 0.25, respectively, over the aforesaid range of lead, and then annealing the resultant composition at a temperature of from about 540° C. to 815° C.

18. A negative electrical conductor consisting essentially of a base constituent consisting essentially of 61.95% to 63.0% lead by weight, balance substantially all tellurium, and not more than of the order of 0.001% by weight of other material except for a member selected from the group consisting of bismuth, tantalum, manganese, zirconium, titanium, aluminum, gallium, chlorine, bromine, iodine, uranium, sodium, potassium, thallium and arsenic, with the bismuth, tantalum, manganese, zirconium, titanium, aluminum, gallium, chlorine, bromine, iodine, uranium, sodium, potassium, thallium and arsenic, in an amount effective to modify the conductivity of the base constituent not in excess of said members as follows: 0.50 tantalum; 0.25 manganese; 0.25 zirconium; 0.15 titanium; 0.10 aluminum; 0.25 gallium; 0.10 chlorine; 0.20 bromine; 0.25 iodine; 0.80 uranium; 0.0002 sodium; and 0.0004 potassium; and bismuth, thallium and arsenic not in excess of from 0.60 to 1.20, from 0.005 to 0.02, and from 0.0008 to 0.002, respectively, over the aforementioned range of lead.

19. A composition consisting essentially of a base constituent consisting essentially of lead and tellurium, the percent by weight of lead being 61.95% to 63.0%, balance substantially all tellurium, and no more than of the order of 0.001% by weight of other matter except for a promoter from the group consisting of bismuth, tantalum, manganese, zirconium, titanium, aluminum, gallium, chlorine, bromine, iodine, uranium, sodium, potassium, thallium and arsenic in an amount effective to modify the conductivity of the base constituent not in excess by weight percent of the lead and tellurium of said promoters as follows: 0.50 tantalum; 0.25 manganese; 0.25 zirconium; 0.15 titanium; 0.10 aluminum; 0.25 gallium; 0.10 chlorine; 0.20 bromine; 0.25 iodine; 0.80 uranium; 0.06 sodium; and 0.10 potassium; and bismuth, tallium and arsenic not in excess of from 0.60 to 1.20, from 0.25 to 1.00, and from 0.07 to 0.25, respectively, over the aforementioned range of lead.

20. A multi-phase alloy consisting essentially of a base constituent consisting essentially of lead and tellurium, the percent by weight of lead being 61.95% to 63.0%, balance substantially all tellurium, having a phase constituting primarily the intermetallic compound lead-telluride and having another phase constituting primarily excess lead, and no more than of the order of 0.001% by weight of other matter, except for a promoter selected from the group consisting of bismuth, tantalum, manganese, zirconium, titanium, aluminum, gallium, chlorine, bromine, iodine, uranium, sodium, potassium, thallium and arsenic, in an amount effective to modify the conductivity of the base constituent not in excess by weight percent of the lead and tellurium of said promoters as follows: 0.50 tantalum; 0.25 manganese; 0.25 zirconium; 0.15 titanium; 0.10 aluminum; 0.25 gallium; 0.10 chlorine; 0.20 bromine; 0.25 iodine; 0.80 uranium; 0.06 sodium; and 0.10 potassium; and bismuth, thallium and arsenic not in excess of from 0.60 to 1.20, from 0.25 to 1.00, and from 0.07 to 0.25, respectively, over the aforementioned range of lead.

References Cited in the file of this patent

UNITED STATES PATENTS

775,188 Lyons ------------------ Nov. 15, 1904

OTHER REFERENCES

"Chemical Abstracts," vol. 47, pages 2591 (d), 3720 (c) and 6246 (a). Published by The American Chemical Society 1953.