July 28, 1942. M. W. WIEGAND 2,290,902

THERMOELECTRIC ELEMENT

Filed Aug. 14, 1939 2 Sheets-Sheet 1

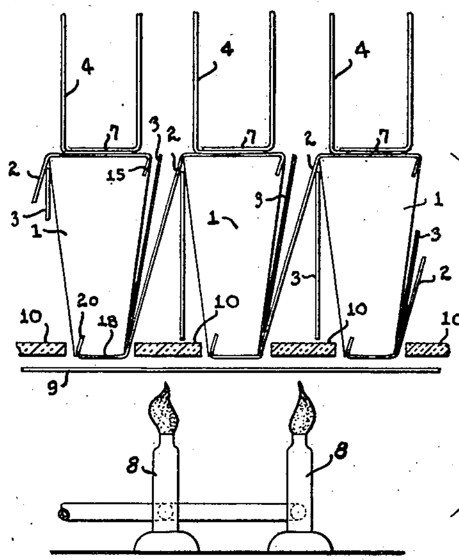

FIG. 1

FIG. 2

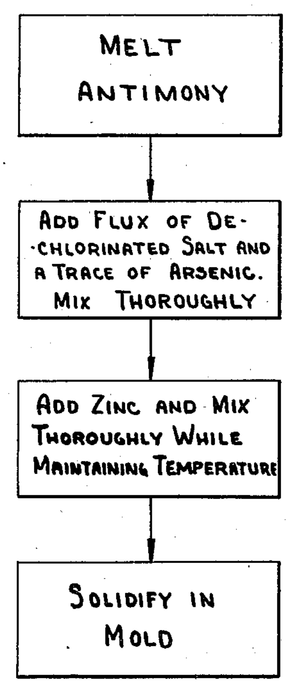

FIG. 3

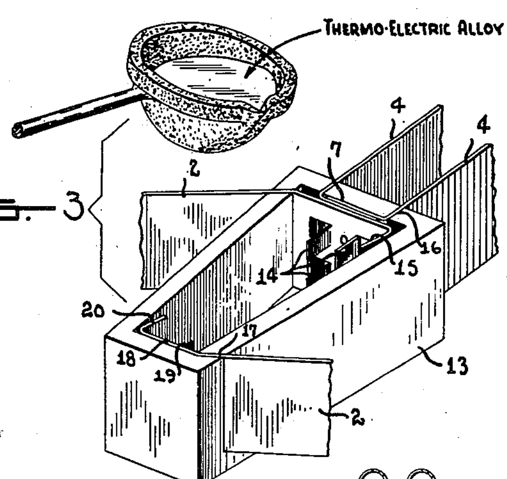

FIG. 5

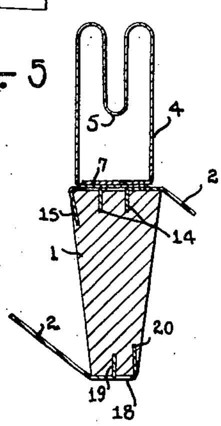

FIG. 6

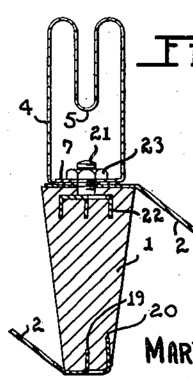

FIG. 4

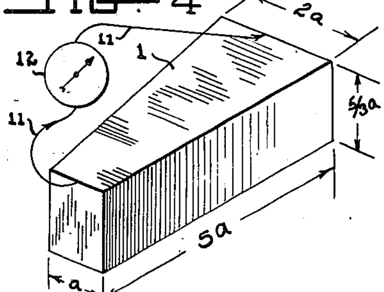

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FIG. 7.

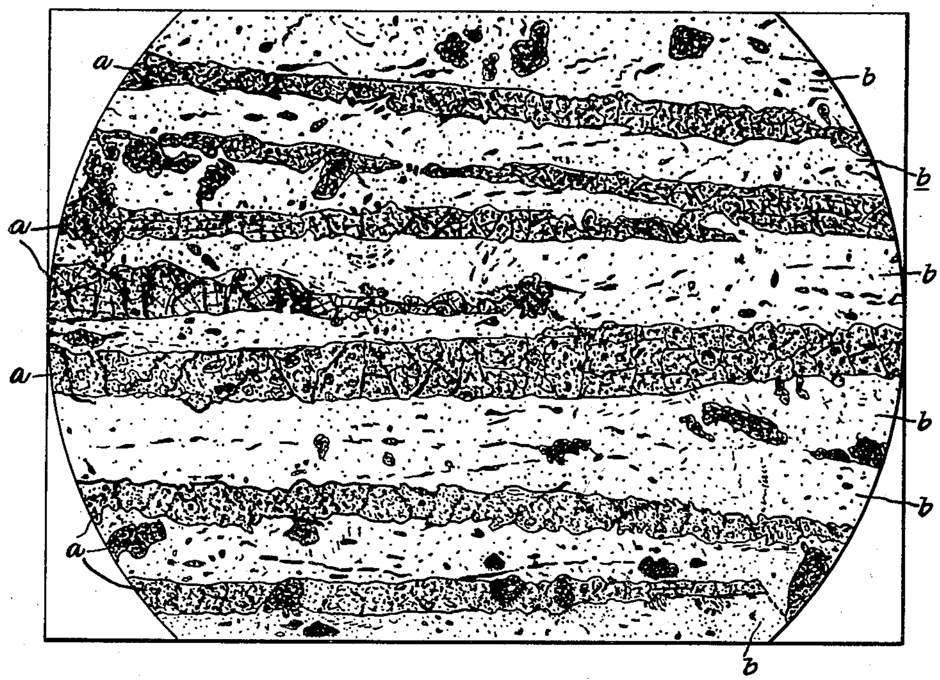
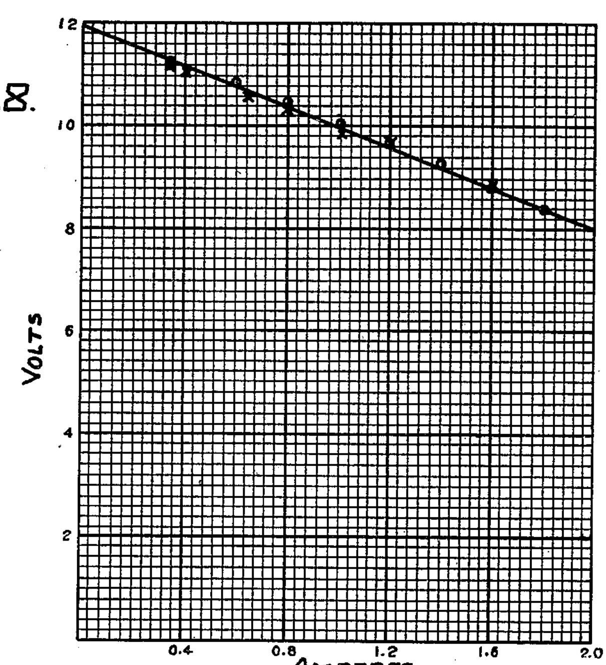


FIG. 8.



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UNITED STATES PATENT OFFICE

2,290,902

THERMOELECTRIC ELEMENT

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Application August 14, 1939, Serial No. 289,956

1 Claim. (Cl. 136—5)

The present invention relates to alloys and in particular to those alloys which exhibit an electric effect upon subjection to heat.

In my application Serial No. 288,408, filed August 4, 1939, entitled "Thermoelectric generators," I have described a thermoelectric generator composed of a large number of thermoelectric units connected in series. These units are constituted of an alloy of antimony and zinc together with connecting strips of a metal known on the market as "copel." It was pointed out in that application that, when the thermoelectric unit is subjected to a readily attainable temperature gradient, considerable thermoelectric energy is produced by the generator. The present invention is directed to the thermoelectric unit as an article of manufacture, also to the method of making the same, although it is to be understood that the alloy employed in the unit has general purposes in the metallurgical arts.

The primary object of the invention is to provide a new alloy which is particularly useful as a highly efficient generator of thermocurrents.

Other objects are to provide a simple and inexpensive method for producing an alloy of this character; to provide a thermoelectric alloy in which the crystalline structure of the metal constitutes a large number of thermocouples; to provide an improved alloy and a method of making the same in which the constituents of the alloy form inter-metallic compounds of a highly sensitive thermoelectric character; to provide a thermoelectric alloy together with terminals of an improved character through which the thermocurrent is taken from the alloy, and to provide an improved method by which the alloy and terminals are secured together to give optimum thermoelectric results; to provide a thermoelectric unit of antimony and zinc with a connector formed of a metal which does not corrode when the unit is heated.

The final object is to provide as an article of manufacture a complete thermoelectric unit including terminals therefor, and ready to be assembled into a battery of units to constitute a thermoelectric generator, and, in addition, a cooling arrangement adapted to be secured to the unit in order to increase the temperature gradient for a given hot junction temperature.

The invention will be better understood when reference is made to the following description and the accompanying drawings, in which—

Figure 1 is a diagram showing the manner in which the improved thermoelectric units may be operated to provide electrical energy.

Figure 2 is a chart setting forth the main steps in the method of making the improved thermoelectric unit.

Figure 3 is a perspective view of a typical mould and a ladle just above, containing the improved alloy, and

Figure 4 is a perspective view of a preferred shape, in which the alloy is cast to give optimum results.

Figure 5 is a sectional view taken across the complete thermoelectric unit including the connectors and the cooling device.

Figure 6 is a view similar to Figure 5, but showing a modified manner of securing the connector to the unit.

Figure 7 is a diagram showing in highly magnified size a typical cross-section of the improved thermoelectric crystal structure.

Figure 8 is a graph plotted against volts and amperes to indicate the performance of a large number of the improved units when connected in series to constitute a thermoelectric generator.

Referring more particularly to Figures 1 and 4, numeral 1 designates a thermoelectric unit or member which has the property of developing a considerable E. M. F. across two opposite faces when the constituents of the unit are of the character and are made in the manner to be described hereinafter. These units preferably have a wedge-shaped form and are cast as a block of uniform thickness as can be seen more clearly in Figure 4. A number of the units are assembled together, with the smaller width portions extending in the same direction so that, when assembled, they form a cylinder of closed configuration and have a thickness determined by the thickness of the unit or block. The sides of each segmental block are electrically insulated from one another, except for a conductor 2 which makes contact with the outer surface of one block and the inner surface of the next adjacent block, as can be seen more clearly in Figure 5. The segmental blocks or units are insulated from one another by means of strips 3 of mica which are interposed between the conducting strips 2 and the converging sides of the blocks.

The strips 2 are secured to the blocks 1 in any suitable manner, but, as will be explained in connection with the moulding operation, are preferably cast in place by means of projecting tabs. As shown in Figures 1 and 5, each unit is provided with a heat-radiating device, preferably in the form of a copper strip or fin 4, bent in the middle, as indicated at 5, and secured in any suitable manner to the upper flat surface of the metal strip 2. In practice, this strip is sufficiently long to provide a pair of overlapping ends, as indicated at 7, these ends being spot-welded together and to the strip 2, as can be seen more clearly in Figure 5.

My investigation of thermoelectric effects extending throughout a long experience has shown that the common characteristics of alloys for thermo-pile use are:

1. They must, in combination of alloys or an alloy and a metal, generate a relatively high potential for a given temperature difference between the hot and cold thermocouple junctions.

2. The electrical conductivity of the metals or alloys should be relatively high to minimize the internal loss due to internal resistance within the couple.

3. Thermal conductivity of the metals or alloys should be relatively low to minimize the temperature increase at the cold junction of the thermocouples due to the heat transference through the alloy or metal from the hot junction. The lower the thermoconductivity the shorter the units can be, and hence the length of the conductors between units can be materially shortened to obtain a given result.

When compounding alloys, there occurs the opportunity by proper choice of metals, proper determination of proportions of each metal in the compound and proper technique of melting, fluxing, pouring and chilling to create in the resulting unit a new phase or structure known as an inter-metallic compound. This composition is usually harder than other compositions of the same metals and of different electromotive force, but not always harder than the metals from which it is made or the other alloys of the same system.

I have discovered an alloy constituted of two metals appearing in a definite range of proportions which when melted toegther in the manner described hereinafter produce stratified layers of two or more inter-metallic compounds which exhibit considerably more thermoelectric effect than either of the metals of which the alloy is composed.

For the material of the block 1, I prefer to employ an alloy which is constituted in part of antimony. The other alloy constituent is preferably zinc with the antimony ranging between 67% to 55% by weight and the zinc between 33% to 45% to make a 100% alloy. As will be explained in connection with the moulding operation, there is also a small amount of flux preferably dechlorinated salt and a trace of arsenic in the alloy. Instead of employing zinc, I may use any metal having a lower melting point than antimony and which provides a malleable matrix for the antimony particles. For example cadmium may be employed in place of the zinc. Silver may be used in place of the antimony. An alloy which has been found particularly satisfactory is composed of 66% antimony, 34% zinc, 10 ounces of dechlorinated salt per hundred pounds of antimony and a trace of arsenic. It will be understood that these percentages may be varied considerably or at least within the ranges set forth above with corresponding results.

As will be explained in connection with the moulding or casting operation, the alloy set forth immediately above meets all of the requirements stated hereinbefore which characterize a highly efficient thermoelectric generator.

The segmental blocks 1 may have any convenient size and shape, but I have found that good results are obtainable when the narrowest width of the segment is approximately ⅜'' and the wider width is approximately ¾'', the segment having a length of approximately 1⅞'' and a thickness of approximately ⅝''. The length of the block as given has been found adequate to provide a readily obtainable temperature gradient when using ordinary cooling means such as air cooling without necessitating an extremely high temperature at the hot junction end. The segments may be made considerably shorter, even to the extent of being two-thirds as short if adequate cooling means were employed to sustain the required gradient. For example, instead of cooling the cold junction by air currents, this junction may be cooled by liquid air, dry ice or forced refrigeration, in which case the length of the segment can be materially reduced. This length seems primarily important only as a factor of permitting adequate resistance to the heat transition from the hot junction to the cold junction end. While I have illustrated these blocks as being of solid construction, it may be desirable to make them of hollow configuration in which case they would weigh less and would cause a reduction of the fragility of the alloy by providing chilled surfaces on the interior of the block as well as on the exterior thereof. Structural reinforcing members could be cast or otherwise inserted in the walls of the hollow blocks so that the thickness of the walls can be still further reduced.

For the electrical conductor 2, I prefer to employ a strip of metal which does not readily corrode upon being heated and which has the same width as the thickness of the block to which it is secured in any suitable manner. Two ways of accomplishing this will be described presently. The metal which I prefer to employ for this purpose is known on the market as "copel," which is constituted of approximately 46% nickel, 54% copper.

When tests on the block of alloy containing antimony and zinc in the percentages above noted and provided with copal connectors at each end, and subjecting the block to a temperature gradient of approximately 600° F., I have obtained a voltage of approximately $\frac{1}{10}$ of a volt. However, it will be understood that as the temperature gradient is increased, for example, by heating the hot junction end to a temperature as high as 1000° F., slightly less than the melting point of the alloy and cooling the cold junction end to as low a temperature as −60° to −100° F., it is possible to increase this voltage very materially. These low temperatures can readily be obtained by apparatus known to those skilled in the art. Assuming that a temperature gradient specifically mentioned above is employed, when thirty of these units are assembled per layer and five layers are held in a rigid structure in any suitable manner, the electromotive force theoretically obtainable between the first and last terminals of the units in the aggregate is $150 \times .1 = 15$ volts. However, due to looseness of contacts and other resistance losses, there is actually available at the terminals 4 of the generator, a voltage of ten to fifteen volts, as indicated by the line "A" on the graph in Figure 8. The voltage varies as a linear function of the current, as the latter is increased up to approximately two amperes. The voltage at the two ampere load is approximately eight volts, and at the one ampere load is aproximately ten volts, giving an electric energy output of between ten and 16 watts. The characteristic "A" has been drawn not only through the performance points (marked "x") as the current is increased, but through the equivalent points (marked "o"), as the current is decreased, showing that the relation between the current and voltage varies as a linear function regardless of whether the current is being increased or decreased. This is of importance in connection with certain kinds of electrical loads.

Many uses for the energy from a generator of this character will readily occur to those skilled in the art, for example, the voltages thus obtained are clearly suitable to the charging of storage batteries or, indeed, for supplying the heater or filament current of commercial radio sets.

While I have described this specific generator as being constituted of five layers of thermoelectric units, it will be understood that any number of layers may be used as desired and any number of segments per layer employed. It is obvious that the improved generator may be designed to contain perhaps thousands of thermoelectric units arranged in any suitable number of layers to produce voltages as high as 440 volts. For these voltages, it is desirable to connect the units in series. However, if desired, the layers may be arranged in parallel or in a series-parallel relation to give any desired relation between the current and voltage values.

It has been found that the optimum results by way of thermoelectric currents and voltages of constant character are obtained by subjecting the hot junctions to radiant energy in the form of indirect heat. This heat may be obtained from any suitable source and, as a typical example, I have shown the hot junctions of each thermoelectric unit as being heated by Bunsen burners 8 positioned under a plate 9 of refractory metal and adapted to radiate heat to the units 1. Heat baffles or barriers 10 are preferably positioned between the units in order to prevent the heat from striking the converging sides of each unit. However, it will be understood that, in practice, these units when assembled may lie close to one another thus eliminating the necessity for the baffles 10. It will be further understood that it is not necessary for the units 1 to describe a cylindrical configuration, because, as indicated in Figure 1, the units may be arranged in a rectilinear formation and still obtain optimum results.

In the event that the units 1 are arranged so close to one another as to form a cylindrical layer, the hot junctions are in juxtaposition to form a cylindrical surface in the aggregate, which may be conveniently heated by a hydrocarbon fuel burner of any type capable of heating the junctions to a temperature of 800° F. to 1000° F. For reasons stated above it is preferred that the flame of the burner does not contact directly with the hot junctions. When using temperatures of this value, the strip 4 should have a length sufficient to maintain the opposite end of the unit or cold junction at a temperature of less than 200° F. The convection effects of ordinary room air have been found to be sufficient for this purpose, but if desired, refrigerated air or fans may be employed in maintaining the cold junction at a sufficiently low temperature.

While I do not wish to be limited to any theory, it is possible that the generation of thermoelectric currents which takes place within the alloys is due, at least in part, to the manner in which crystals of antimony and zinc occur in the unit during the moulding process which will be described presently. The crystal arrangement may be such that zinc forms a malleable matrix for the antimony, and the particles of zinc and antimony so orient themselves as to form thermocouples, all of which are poled in a series manner to cause their respective electromotive forces to add. These electromotive forces in the aggregate are available between any two surfaces of the alloy when the latter is subjected to a temperature gradient. It is entirely possible that at the melting heats and proportions of the metals used instead of a simple alloy of antimony and zinc being formed in which the zinc is the matrix, one of two compounds of zinc and antimony structurally separated into a matrix and crystal is obtained. One of these compounds may be constituted of Zn_3Sb_2 (three molecules of zinc, two molecules of antimony), which chemically is composed of 44.6% zinc and 55.4% antimony and melts at 1051° F., while the other is Zn Sb (equal number of molecules of zinc and antimony, i. e., equal in bulk but not weight), which is 65.1% antimony and 34.9% zinc by weight and melts at 998° F. The first of the two mentioned compounds, therefore, has a complex structure in that the zinc and antimony molecules do not appear in equal proportions. The other of the two compounds has a simple structure in that molecules of zinc and antimony appear in equal numbers.

The structural characteristics of the arrangement of these compounds in the block is shown in the microphotograph, a copy of which in magnified form, is illustrated in Figure 7. The dark strata indicated at *a*, depicts the compound having the low zinc content, i. e., the ZnSb compound, while the light strata indicated at *b*, depicts the compound having the high zinc content, i. e., the Zn_3Sb_2 compound. It is apparent that the simple and complex metallic compounds alternate with one another and there is some experimental basis to indicate that the improved thermoelectric effect is obtained at the boundaries between each pair of compounds. These boundaries are broadly suggested by the full lines running across the figure and separating the dark portions from the light portions of the sketch. Thus, myriads of thermoelectric couples exist along the numerous boundaries, each couple comprising metallic compounds of dissimilar character but both containing zinc and antimony in different proportions. In case other metals are used instead of antimony and zinc, as explained hereinbefore, similar layers in alternate arrangement will be formed by the improved molding process described hereinafter, to provide thermoelectric effects throughout the long boundary lines which separate one inter-metallic compound from the other inter-metallic compound.

My invention, therefore, contemplates the use of any combination of metals in the thermoelectric series, which upon being melted together, as explained hereinafter, forms striations or layers of different inter-metallic compounds separated by a thermoelectric junction at the boundaries between the compounds.

But regardless as to whether the theory in which the zinc forms a matrix for the antimony or the theory in which the zinc and antimony go into a solution to form striations of different compounds by which the improved thermoelectric effects are obtained is correct, it is a fact established by numerous tests that when 30 of the units as described hereinbefore, are connected in series, electromotive force and current values, such as indicated in Figure 8 are obtainable when employing a temperature gradient as little as 600° F. It will be understood that when greater temperature gradients are employed, for example, when the hot junctions are heated to approximately 1000° F., and the cool junctions are cooled to a temperature of −60° F. to −100° F. in any suitable and well-known manner, considerably greater voltages and currents are available. It will also be understood that the relation between the voltages and currents can be varied by changing the electrical connection of the units from series to parallel or series-parallel.

I have obtained optimum results by way of electromotive force and current values when employing units of the size and shape described hereinbefore, but experiments have shown that the thermoelectric property is inherent in the alloy regardless of its shape or size. I have also found that, in general, as the size of the unit is increased, the current is increased in a corresponding degree, but the voltage does not increase in the same proportion. For the most satisfactory results, it is desirable to maintain the general proportions between the various dimensions, also the shape of the unit as exemplified in Figure 4. Assuming that the width of the narrower portion is a, the width of the wider portion should be $2a$; the length of the unit should be $5a$ and the thickness of the unit should be $5/3a$.

The manufacture of the unit and desirable method of securing the strip connectors thereto are illustrated in Figures 2 and 3. A mold 13 of a refractory metal is provided, having an interior of the shape desired for the segment. The strip 2 which connects with the outer surface of the unit is preferably provided with four vertically extending tabs 14 pressed out of the metal, as indicated in Figure 3. This strip is of sufficient length to extend flatwise against the end of the mold leaving an end portion 15 which bears against the side of the mold and is bent at an angle with respect thereto.

In practice, the fins 4 are spot-welded to the portion of the strip 2 which lies flatwise against the end of the mold, these fins being received in a slot 16 provided in the end of the mold. The other strip 2 passes through a diagonal slot indicated at 17 in the edge of the mold and terminates in a flat portion 18 (Figure 3) which contains a pair of inwardly extending tabs 19. The end portion 18 terminates in a bent portion 20 which is bent at an angle with respect to the side of the mold.

For the manufacture of the thermoelectric unit, I prefer to first test the antimony in its raw state by flame to determine whether any arsenic is present. A trace of arsenic is present in some antimony and is needed in the fusing of the crystal, its action being that of a flux to assist the formation of many minute crystals during the melting of antimony. If there is no arsenic in the metal, a small amount is added in the next step which is to melt the antimony. This is done at 1350° F., at which temperature, the metal is light red in color. There is then added a flux which breaks up the antimony into the finest possible condition and drives off any gas that is present in the molten mass. Suitable fluxes for this purpose are ordinary salt, magnesium, beryllium and vanadium. From the standpoint of cost and result, experiment shows salt to be the best of these fluxes. However, before it is introduced into the molten antimony, it must be heat treated for a couple of hours at a temperature of 800° to 900° F. to dechlorinate the salt. After this treatment, the salt is dark brown in color, and it is added to the antimony in a proportion of ten ounces to a hundred pounds of antimony.

Zinc is added with the temperature remaining at 1350° F. and its addition should be accompanied by extreme vigilance to prevent appreciable lowering of the temperature or too rapid a mixing of the metals. The final step in the process is the pouring of the mixture into the mould 13, as indicated by the ladle shown in Figure 3, the metal being maintained at a temperature of approximately 1350° F. during this step.

The molten metal will fill up the entire mould, encompassing the tabs 14, 19 and flowing between the strip extensions 15, 20 and the side of the mould, thus securely holding the strips 2 and the heat-radiating fins 4 to the unit 1. Inasmuch as the tabs, in extending inwardly into the cast metal, tend to reduce the resistance of the latter slightly in the longitudinal direction, the tabs should not be too long and yet they must have a sufficient length and width securely to hold the strip 2 in place. I have found that, when the block 1 is of the dimensions set forth hereinbefore, particularly good results are obtained by way of securing the strip 2 in the block without reducing the resistance to an excessive degree when the tabs have a dimension of approximately 1/8", i. e. as measured in the vertical direction, and 5/32" long as measured in the horizontal direction. As the size of the unit 1 is increased, the length and width of the tabs should be increased accordingly.

In practice, a number of thermoelectric units 1 are cast simultaneously in a multiple mould, even as many as thirty or more to form one of the five layers of a thermo-generator, as described hereinbefore. If desired, a number of individual moulds 13 may be employed for this purpose, and, after being cast to form, as indicated in Figure 3, the adjacent units 1 may be brought together, as shown in Figure 1, and insulated from one another by their mica strips 3.

Instead of providing the strip 2 with tabs which are cast into the metal, other fastening means may be employed. Thus, in Figure 6, I have shown a stud 21 secured to an anchor 22, the latter being cast in place and the strip being held to the stud by a nut 23. In order that the metal of the unit 1 will not attack the stud 21, the latter should preferably be silver-plated. It will be noted that the stud-and-nut arrangement may be employed, if desired, to hold the fin 4 in place. It will be noted in Figure 6 that the stud-securing means is illustrated as being employed only for securing the strip 2 to the upper face of the unit 1. I prefer to use this securing means only at the cold junction end of the unit so that, in the figure, I have indicated the tab method of securing the strip to the unit at the hot junction end.

Figure 2 illustrates, by way of a flow diagram, the main steps of the method for producing the improved thermoelectric alloy, i. e., an alloy which, upon being heated, exhibits thermoelectric effects between any two surfaces thereof. Upon fracture, the alloy will be found to have a marked crystalline appearance, is somewhat brittle and is slate gray in color.

It has been pointed out that when antimony and zinc in the proportions stated are melted and cast as described hereinbefore to form a block of thermoelectric material, an alloy is produced which has a new phase or structure known as an inter-metallic compound. This compound is in addition to the ordinary Sb-Zn, and is characterized by being composed of three molecules of zinc and two molecules of antimony. An alloy in which each of these compounds exists generates a relatively high thermoelectric potential for a given temperature difference between the hot and cold thermocouple junctions. Such an alloy also has a relatively high electrical conductivity by which the internal loss due to the internal resistance within the alloy is minimized. Finally, the thermoconductivity of the alloy is relatively low so that the temperature increase at the cold junction of the thermocouples due to the heat transferance through the alloy from the hot junction is minimized.

While I have set forth the constituents of the improved alloy as comprising antimony-zinc, antimony-cadmium, silver-zinc and silver-cadmium combinations it will be understood that in accordance with my invention, other combinations of metals or pure metals may be employed which have the high potential, high electrical conductivity and low thermoconductivity comparable to the corresponding characteristics of the alloys specifically mentioned. My invention also contemplates the use of metals, either in the pure or alloy form which upon being melted and cast or moulded as referred to hereinbefore produce inter-metallic compounds throughout the metal or alloy which is harder than other compositions of the same metals and which exhibits a higher thermoelectromotive force than the metals from which it is made or the other alloys of the same metallurgical system.

Again, it is desired to state that the invention is not limited to the use of "copel" as the connecting strip between the thermoelectric units as this metal or alloy may be replaced by any metal or alloy which does not corrode at the temperatures employed in heating the hot junctions. In addition, the substitute alloy or metal should appear at a position in the thermoelectromotive force series of elements which is more positive or less negative than antimony or than the combination of antimony-zinc or the equivalent compounds of these last two mentioned metals which have been set forth hereinbefore. For example, a metal known on the market as "constantan" may be employed in place of the copel; constantan is composed of 40% nickel and 60% copper. I have obtained particularly good results by way of a higher thermoelectromotive force by employing a copel strip secured in any suitable manner to a block of antimony-zinc in which the antimony and zinc have the range of proportions set forth hereinbefore.

It will be understood that the use of the improved antimony-zinc alloy is not limited to a thermoelectric uint but has many other applications among which may be cited by way of example its use as an effective hardener when added to zinc, to aluminum alloys and to cast iron. The improved alloys may also be used for inexpensive jewelry, as with proper handling, the alloy comes from the moulds with brilliant and beautiful colors.

It will be understood that I desire to comprehend within my invention such modifications as come within the scope of the claim and the invention.

Having thus fully described my invention, what I claim as new and desire to secure by Letters Patent is:

An article of manufacture comprising a block of thermoelectric alloy, electrical conductors provided with a plurality of vertically extending tabs pressed out of the metal and which enter the block at each end whereby the conductors are rigidly secured to the block, and a strip of metal in the form of a closed loop bent reversely at the middle and having its ends in overlapping arrangement and secured by spot welding to the overlapped portion of the conductors at one end of the block.

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