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G. R. WATSON ET AL

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METHOD OF MAKING ELECTRICAL HEATER BARS

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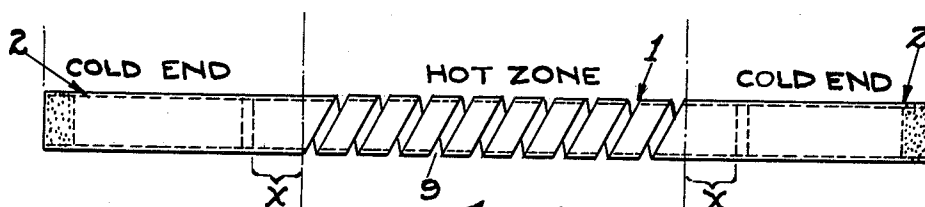


Fig. 1.

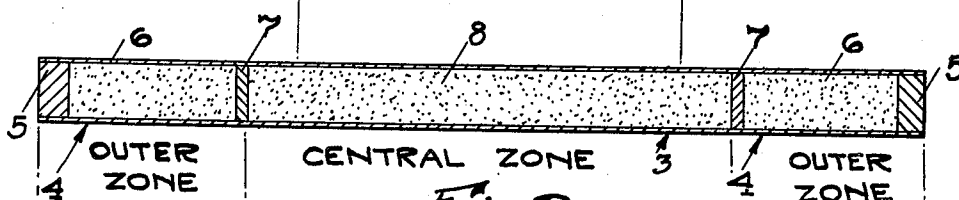


Fig. 2.

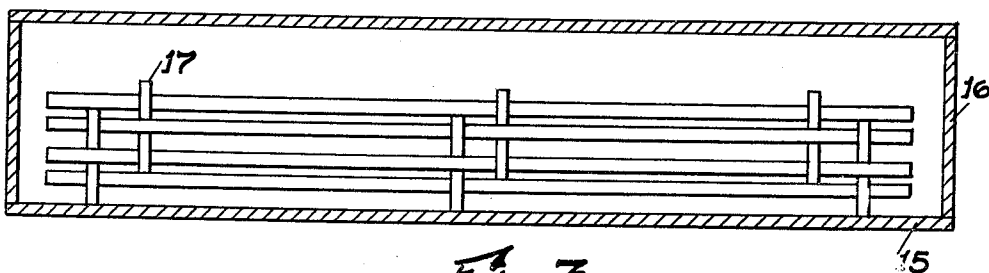


Fig. 3.

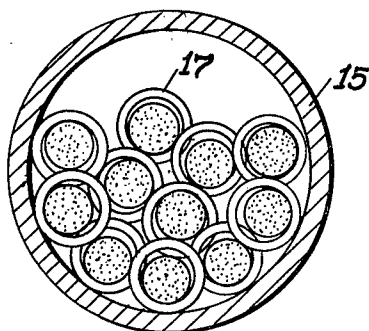


Fig. 4.

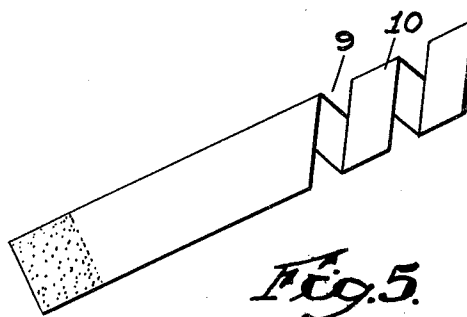


Fig. 5.

INVENTORS
George R. Watson
John I. Fredriksson
By Allan R. Redrow ATTORNEY

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METHOD OF MAKING ELECTRICAL HEATER BARS

George R. Watson, Chippawa, Ontario, and John I. Fredriksson, Niagara Falls, Ontario, Canada, assignors to Norton Company, Worcester, Mass., a corporation of Massachusetts

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This invention relates to a method of making electrical heater bars and more particularly to a recrystallized silicon carbide bar impregnated with a molybdenum silicide composition in the hot zone.

One object of the invention is to make an improved electrical heater bar capable of use in air at temperatures up to 1700° C. for unusually long periods of time. Another object of the invention is to make such heater bars with a more exact control of electrical resistivity. Another object is to provide heater bars of such characteristics that they can be made by practical and inexpensive methods. Another object of the invention is to provide an improved method for making heater bars.

Most furnaces are designed to have the heater bars placed horizontally but certain bars on the market, such as those formed of solid molybdenum silicide, cannot be placed horizontally because they sag in operation at high temperatures. Either these bars have to be supported somewhere along the hot zone which is inconvenient, or they have to be placed vertically, which means they cannot be used in most furnaces now in operation. Our bars are free from these objections.

Our bars can be made out of ordinary grades of silicon carbide grain, whereas it has heretofore been necessary to use very pure silicon carbide which is from light green to nearly clear in color. Another object of the invention is to produce electric furnace bars which can operate in air up to 1700° C. for thousands of hours without requiring the use of special electrical transformers in the electrical supply circuit.

Other objects will be in part obvious or in part pointed out herein.

In the accompanying drawings,

FIGURE 1 is an elevation of a finished heater bar made according to the invention;

FIGURE 2 is a sectional view of a tube which is an intermediate form used in the production of the heater bar prior to impregnation and spiral cutting of the tube;

FIGURE 3 is a view of a graphite sleeve adapted to hold the loaded tubes shown in FIGURE 2 during performance of the molybdenum silicide and silicon impregnation step simultaneously of the center and outer zones of a number of tubes;

FIGURE 4 is an end view of the graphite sleeve of FIGURE 3 showing the loaded tubes spaced apart therein; and

FIGURE 5 is a detailed view showing the spiral cut in the wall of the tube to form the helix which constitutes the hot zone of the resistance bar of this invention.

Briefly, the heater bar of the present invention is constructed from a hollow tube and preferably in the manufacture, the hot zone 1 is formed integral with the cold ends 2. In this instance, the entire bar is made of recrystallized silicon carbide suitably impregnated to produce the desirable electrical characteristics required in the cold ends to feed current into the hot zone and to produce a hot zone which may be cut spirally to form a helically shaped resistance element having a specified resistance to produce the desired temperature range with a certain current flow.

It is known to produce resistance elements of recrystallized silicon carbide, but such bars cannot be heated

to high temperatures in the order of 1600° C. to 1700° C. because the silicon carbide oxidizes. We have found, however, that a silicon carbide matrix can be made to support an impregnant which becomes the conductor and also protects the silicon carbide from oxidation at temperatures as high as 1800° C. To accomplish this the silicon carbide of the central zone 3 of the resistor bar of our invention is impregnated with a molybdenum silicide compound while the outer zones 4 may be impregnated with the same silicide compound but preferably with silicon. As will appear more fully below, the impregnation of the several zones may be accomplished by plugging the end of the tube as shown in FIG. 2 with a plug 5 and packing the one cold end section with powdered silicon 6. A dividing plug 7 may be inserted on top of the silicon to divide the outer zone 4 from the central zone 3. The interior of the central zone then may be packed with a molybdenum silicide compound 8 and after it is full a second plug 7 may be inserted between the central zone 3 and the second outer zone 4. The second outer zone then may be filled with silicon 6 and the tube closed with another plug 5.

Preferably, silicon is used in the outer zones 4 to improve the conductivity of the low temperature ends of the cold ends 2. This is conventional, and while other impregnants, including molybdenum silicide compounds, may have better characteristics for conductivity or otherwise, silicon has been found to be the most practical cold end impregnant to date. Silicon may be used in this area of each of the cold ends since the temperature normally is maintained relatively low. Silicon is refractory enough to stand up under the temperatures normally encountered at the exposed ends of the resistor bars when they are subjected to normal operation; however, as the temperature along the cold end increases toward the central zone and where the cold end is connected to the hot zone, a different impregnant has been found to be more useful.

The hot zone 1 of the present invention is designed to operate at much higher temperature ranges than the temperature to which the normal resistor bar may be subjected, and it has been found that a molybdenum silicide compound when impregnated in the bars, as will be described below, serves to protect the hot zone 1 against oxidation damage. It has been found that with our construction, a hot zone can be produced which may be operated continuously above 1500° C. and at temperatures as high as 1800° C. for many hours without apparent damage.

In constructing a bar in accordance with our invention, the principal raw material used for making the hollow bars is silicon carbide. Any grade of silicon carbide can be used. This is crushed to 100 mesh and finer and then further reduced in particle size such as by dry milling to less than 50 microns in size, but the invention is not to be deemed limited to this sizing.

Another raw material for the manufacture of these electric furnace bars which are also called rods is molybdenum disilicide, MoSi₂. We prefer a rather pure variety of this material at present but probably the impurer varieties can be used to produce inexpensive bars where the requirements for the bars are not so rigid. Very pure molybdenum disilicide can be obtained having a total of more than 99% molybdenum and silicon. But this is not necessarily all MoSi₂.

It contains probably also other silicides in the form of Mo₃Si and Mo₅Si₃ which may be the only others present. But other silicide compounds with molybdenum in the ascending order of amount of silicon are respectively empirically Mo₁₅Si₅, Mo₁₅Si₁₀ and MoSi₂ or Mo₁₅Si₃₀ and these also may be present. Also there may be some free silicon in this silicide material. Any material having not more than 37% Si and total Mo and Si at least 90% may

be used, but for the best results at least 98% and for the very best results at least 99% total Mo and Si, is preferred in our invention. In the claims all of these usable materials will be called "molybdenum silicide."

A third raw material is silicon, which preferably contains a small amount of boron carbide to lower further the resistivity of the silicon impregnated portion of the bars. The purity of both the silicon and the boron carbide respectively should be at least 90%. The percentage of boron carbide relative to silicon in this mixture should be between 0.078% and 5%. The particle sizes of this mixture can be anything so long as the boron carbide can dissolve completely in the molten silicon and as long as sufficient material can be loaded into the bar to impregnate the pores completely.

Similarly, the particle sizing for molybdenum silicide compound really is not critical so that really any sizing at all can be used provided enough material is provided to fill completely the pores of the hollow bar during the impregnation step.

It will be obvious to those skilled in the art, that some moisture, temporary binders and extrusion promoters also may be used.

The operations of making an electrical resistance bar in accordance with the invention are as follows:

Silicon carbide, to form the hollow bar, is reduced to the desired particle size. Then it is mixed with a binder and made into a hollow rod which preferably is cylindrical. This hollow rod then is baked to remove most of the binder in order to avoid blistering, etc. But conceivably this can be combined with the next operation so long as the temperature-time curve is adjusted properly.

The next operation is recrystallizing of the silicon carbide. This is done by heating the bar to an optimum temperature of about 2100° C. under reducing conditions. At this temperature under these conditions the silicon carbide particles grow together which is called recrystallizing. They do not melt because silicon carbide does not melt under ordinary pressures nor in any combination of temperature and pressure so far as we are aware. Silicon carbide can be recrystallized at any temperature between 1650° C. and up to about 2400° C. At about 2500° C. to 2650° C., the silicon carbide dissociates. The actual temperature of recrystallization is a function of the fineness of the silicon carbide.

These operations so far have produced a hollow bar, cylindrical inside and outside, of recrystallized hexagonal silicon carbide. This bar then is impregnated with the molybdenum silicide compound throughout its central zone and its outer ends are impregnated with silicon with or without boron carbide. This impregnation operation may be done in the following manner:

A refractory plug 5 made of any suitable material such as carbon or SiC or the like is inserted into one end of the bar. The bar then is up-ended and filled to the level of the end of one outer zone 4 with silicon 6 with or without the added boron carbide. A refractory plug 7 then is inserted to close off the filled outer end portion. The center zone 3 of the hollow bar then is filled for the distance of the entire length of the central zone with the molybdenum silicide compound 8. Another plug 7 then is inserted at the other end of the central zone. There remains room enough for the other outer zone 4 which then is filled with more silicon 6 with or without the boron carbide and then another plug 5 is fitted into this end of the hollow bar.

The next step is completed by melting the silicon and molybdenum silicide compounds filled into the bar. To accomplish this the loaded bar is heated again to a temperature in the order of 2000° C. which melts the silicon and molybdenum silicide compounds, the former dissolving any boron carbide entrained therewith as it flows into the pores of the bar. The melting point of silicon is 1420° C. The melting point of pure MoSi₂ is given as 2030° C., that of Mo₃Si₂ and Mo₃Si as 2090° and 2050° C. Actually neither the molybdenum silicide compound

nor the silicon will liquefy well to impregnate the bar by capillary action until it is heated to above about 2100° C. It has been found that best results have been attained at this range and too high a temperature results in a non-uniform distribution of the molybdenum silicide compound. It is preferred therefore to just heat the bars to a little above the liquefying temperature of the silicide compound.

After the outer and central zones of the bar have been impregnated thoroughly with the molten materials which flow into the pores in the bar and throughout the wall of the tube to the outside, the bar is cooled and thereafter the electrical properties of the hollow bar are determined. After finding the resistivity value of the center zone 3, the hot zone portion 1 within the center zone is marked off and a spiral cut 9 is made to form the hot zone into a long ribbon-like conductor in the form of a helix 10. Since the resistance per unit of length of the material of the center zone 3 can be determined, it is possible to design the pitch of the spiral cut 9 to produce a resistance heating element having the desired electrical resistance within very close tolerances. The spiral cutting can be done with a diamond cut-off wheel. Although there are other optional steps and variations of the described steps which can be used, the foregoing explains the preferred manufacture of our bars and in following this practice, the electrical characteristics of each of the bars can be designed to meet a very close specification.

In accordance with the above we provide a resistance bar having a molybdenum silicide impregnated hot zone, and cold ends each having a composite structure including the outer zone 4 impregnated with silicon and a portion of the central zone 3 impregnated with molybdenum silicide.

We have made bars impregnated entirely with a molybdenum silicide compound. In use, however, the molybdenum silicide compound oxidizes readily at temperatures below 1000° C. The molybdenum oxide tends to vaporize leaving the silicate in a powder form. It is, therefore, necessary in order to prevent the deterioration of the molybdenum silicide impregnated outer portion of the cold end to provide it with a protective coating which will not crack upon being subjected to the heat normally encountered in the operation of the cold end. A borosilicate glaze has been found satisfactory for this purpose. Such a glaze can be accomplished by simultaneously impregnating the cold ends with a molybdenum silicide compound and boron carbide under reducing conditions. Thereafter when the bar is in use, the boron carbide and silicide react at the relatively lower temperatures at which the cold end operates, to form a borosilicate glaze.

Also the composite silicon and boron carbide outer zone impregnation coupled with molybdenum silicide impregnation in the portions x of the central zone where the cold ends operate at temperatures above 1000° C., has been found to be most satisfactory. This composite cold end structure makes available a cold end having the known characteristics of the conventional cold ends of present day silicon carbide resistor bars. The electrical connections to the bars of this invention thus can be completed most easily. The portions x as well as the remainder of the central zone, however, are protected by the molybdenum silicide impregnation and throughout all portions of the bar operated at temperatures above 1000° C., a protective silicate glaze is formed which fully protects the silicon carbide matrix from oxidation.

Another feature of our invention is the heat transmission barrier provided by plugs 7 which separate the outer zones 4 from the central zone 3. These plugs define approximately the 1000° C. point in the cold end and are left in place within the bars upon the completion thereof. The radiant energy generated at the hot zone 1 impinges upon plugs 7 at each end of the central zone

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3 of the bar when in use and the plugs serve as very effective radiation shields to reflect the radiant energy back which might otherwise escape into the outer zone 4 of the bar. This reflective action allows the cold ends 2 of the bars to operate at much lower temperatures, which is highly desirable.

EXAMPLE

For the manufacture of a resistance rod 29" long with cold ends of 8.5" and a hot zone of 12", an inside diameter of $\frac{1}{2}$ " and an outside diameter of $\frac{3}{4}$ ", the following was done:

A quantity of green silicon carbide of the hexagonal variety in lump form analyzing more than 99% pure, was crushed to pass through a 100 mesh screen. Ten thousand grams of this material was loaded into high speed steel ball mills. Milling for 40 minutes gave the following sizing:

Table I

Microns	Percent
100-150	2
75-100	4
50-75	6
35-50	15
25-35	20
15-25	25
7-15	17
3-7	10
1-3	1
Less than 1	Trace

Eleven hundred and forty grams of this silicon carbide then was mixed with 24 grams of corn flour, trade mark Cere-Amic, 36 grams of poly vinyl alcohol, trade mark Elvanol 70-05, 75 milliliters of glycerine and 120 milliliters of water. Actually the silicon carbide, corn flour, and alcohol were mixed first, then the water was added and the materials were mixed further, then the glycerine was added and the materials were mixed further. This made an extrudable mix. All mixing was done in a muller type mixer.

We had an extrusion press, the cylinder of which could be evacuated. A vacuum of over 25" was created in the cylinder and maintained for five minutes before extruding and the vacuum was maintained during extruding as well. Extrusion of the mix was done at about five tons on the $\frac{2}{4}$ " diameter die plunger.

Naturally more mix was put into the cylinder or die than was required for one bar and as the extrusion proceeded, lengths were cut to make bars 29" long. Changing the singular now into the plural because more than one bar was made at a time, the bars then were air dried at room temperature over night. The next day they were transferred to an oven and dried at 150° C. for four hours. Then they were transferred to a furnace and heated to just above 250° C. for four hours to remove all but 10% of the binder and extruding aid (glycerine). This furnace had an air atmosphere.

The bars then were fired under reducing conditions at a temperature of about 2100° C. to effect recrystallization of the SiC in the bars. Having been dried thoroughly and charred by the previous steps, the firing cycle is not critical at all. The 2100° temperature can be held for any length of time so far as we know. Under the reducing conditions the temperature can be raised just about as fast as possible without doing any harm and the bars are held for a reasonable length of time at 2100° C. as is well known, or at lower temperatures which approaches that temperature for a considerably longer time. This is to give the SiC particles a chance to recrystallize or grow together. But as all this is established practice, we do not have to give any more details.

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The furnace actually used for recrystallizing the bars was a furnace such as that thoroughly described in U.S. Patent 2,125,588. The bars were fed slowly through this furnace at the rate of 30" an hour, the total sintering time from the start to the time when the bars were completely out of the furnace was 3 hours and 40 minutes and the central portion of the long graphite tube of the furnace was held at 2100° C. The furnace tube is 64" long.

To form the plug 5, a paste of this same silicon carbide was made with corn flour binder and plugged into one end of each of the sintered bars. There is nothing very critical about the length of the plugs 5 but we did make plugs that were only $\frac{1}{2}$ " long. After air drying for about an hour, any cracks in any of the plugs were patched with the same paste and the bars then were dried in the oven for two hours at 150° C. to remove the moisture from the plugs.

The bars then were up-ended and filled first with silicon and boron carbide mixture 6 to the top of the first of their respective outer zones 4 to a height of about $6\frac{1}{2}$ ". One-quarter inch long SiC plugs 7 were then inserted at the end of the filled outer zone and dried in each of the tubes, then the central zones 3 each were filled with the molybdenum silicide compound 8 to a height of about $15\frac{1}{2}$ ". Other $\frac{1}{4}$ " SiC plugs 7 then were inserted and dried in the tubes and the second of the respective outer zones were filled with the said first silicon and boron carbide mixture, leaving room for $\frac{1}{2}$ " SiC plugs 5 made from the SiC flour paste at their tops.

To accomplish this filling, it is easy to measure with a rod having scale marks which can be used also for tamping each mixture lightly which was done. The percentage of the boron carbide relative to the silicon was 1% in this mixture. The particle size of the molybdenum silicide compound was minus 30 mesh and of the silicon and boron carbide was minus 30 and minus 100 mesh respectively.

The filled bars then were loaded, up to 12 at a time, in a suitable graphite sleeve 15 fitted with graphite covers 16 as shown in FIG. 3. They were spaced apart by the enlarged graphite spacers 17 to avoid the sticking together of the bars. This sleeve then was placed in one end of the tube of the above described furnace used for recrystallizing the SiC, which furnace had a $\frac{5}{8}$ " I.D. In following conventional practice, the interior of the furnace was filled with similar graphite sleeves with the same weight of material (SiC bars, for instance) per unit of length as the sleeve to be sintered. This "dummy load" insures that the heat balance in the furnace remains constant. The furnace was heated in 40 minutes to 2080-2100° C. and the dummy load was soaked at this temperature for half an hour, then the tube containing the bars was passed through the hot zone of the furnace at 30" per hour while the furnace was kept at the same high temperature. In production runs, successive loads may be fed through a furnace of this type; however, the rods of this example carried in a sleeve 15 were removed from the end of the furnace and upon cooling the bars were removed from the sleeve. The graphite spacers were broken loose easily with finger pressure. This heating procedure completed the impregnation of the bars.

In following the usual practice, the tip ends of the cold ends of furnace bars are coated with aluminum by means of a flame spray gun for better electrical contact.

In some instances, a portion of the silicon impregnating material went through to the outside wall of the tube and solidified in the form of small beads which were scraped easily from the surface. The bars then were complete except for the spiral cutting.

The electrical values of the impregnated bars then were determined and the 12" hot zones were cut spirally to a pitch of 0.29" with a diamond cut-off wheel. The cuts, of course, went all the way through, meaning that the walls were cut through to the inside. Thus the electrical length of the conductors which formed the hot zones were

increased greatly. The width of the cut was 0.055", as shown at 9 in FIGURE 1 and FIGURE 5.

These bars each had an average resistance of 1.11 ohms in their hot zone and a total cold end resistance of 0.081 ohms.

Electrical heater bars are wanted in many different sizes with many different resistances for the hot zone of each size. An equation relating all the factors involved is shown below:

$$R = rL \frac{(Pi(OD + ID))^2 + 4P^2}{(PiP)(P - S)(OD^2 - ID^2)}$$

where

R=resistance

r=resistivity

L=length of hot zone, measured along the axis of the bar

Pi=3.1416

OD=outside diameter

ID=inside diameter

P=pitch of spiral, length of one turn measured along the axis

S=width of groove between spirals

The resistivity of the hot zone of bars made according to the above example is .001 ohms cm. plus or minus 10% variation. It is easily possible, however, to design a variation in the resistivity of the hot zone to make it fall between .005 and .0005 ohms cm. by variation of (a) porosity and molybdenum silicide content, (b) grade of molybdenum silicide and (c) the grade of silicon carbide used, the resistance generally being lowest when pure SiC is used. This variation range meets all present requirements, and the ohmic resistance of a hot zone of a given length can be varied widely by altering the pitch of the spiral cut into the tube to form the hot zone.

We have tested furnace bars made as herein described by service tests at temperatures between 1650° C. and 1700° C. and after 900 hours in this service they were inspected and found to be apparently in perfect shape. A portion of the molybdenum silicide impregnated into the central zone was exposed on the surfaces of the helix throughout the hot zone and was converted to an oxidation resistant coating on the surface at high temperatures in the form of a protective siliceous glaze.

In the outer end zone, in place of boron carbide together with silicon we can use titanium boride or zirconium boride. As is known, boron carbide is also carbon boride and therefore it is related to titanium boride and zirconium boride. Either of the titanium boride or zirconium boride compounds can be substituted for the carbon boride and mixtures can be used to improve the silicon impregnant. The limits are from 0.078% to 5% of boron on the free silicon in the cold end. Other borides can be used as it is the boron in the cold end which reduces the resistivity thereof. Presently known borides are those of carbon and of the transition metals which are titanium, zirconium, hafnium, vanadium, columbium, tantalum, chromium, molybdenum and tungsten. Free boron can be used but it is expensive. In the claims "boron" means either free or combined. Wherever zirconium boride is mentioned it is to be understood as containing the normal amount of hafnium boride with which it is almost always associated.

Many variations may be made in this invention. For example, it is utterly immaterial to the method what apparatus is used so long as the various steps described are carried out. Furthermore, many of the sub-steps can be modified or eliminated entirely.

Any conventional binder can be used. Also any lubricant or extrusion promoter, can be used. The tubular shapes may be formed in any way in which they can be manufactured within the broadest scope of the invention

and so far as these articles are concerned. Molding, ramming and slip casting are other shape forming methods that can be used.

In accordance with the invention, the percentage by volume of recrystallized silicon carbide in the bars is from 55% to 85%. The remainder of the material by volume is the impregnating material with the exception that there may be a few unfilled or partially filled pores.

Instead of forming the cold ends integral with the hot zone as described above, the cold ends may be formed separately of any conventional design and welded to the hot zones as is well known and has been practiced commercially for years.

For producing silicon carbide cold ends containing silicon, the patent to Heyroth No. 2,431,326 can be followed. To weld them onto the hot zone the patent to Kelleher 1,588,473 can be followed. Further details will be found in the patent to Heyroth 2,319,323. In accordance with these patents the cold ends were not tubular but they could be. As there are many different ways, such as are described in the patents referred to for making a silicon carbide body containing silicon, the word "impregnated" in the claims means simply that the free silicon is in the silicon carbide.

The temperature range found most effective for accomplishing the impregnating of SiC with silicon is from 1800° C. to 2600° C. and the best results are attained in the range of from 2000° C. to 2200° C. With the use of temperatures below 1800° C. the silicon will not easily wet and penetrate the silicon carbide, and above 2600° C. it tends to vaporize so that too much of it will escape. If the silicon does not wet the silicon carbide so as to penetrate it, on cooling the silicon becomes a layer of solid silicon in the bottom of the hollow tube and in use may melt and be lost.

The disclosure headed "Example" gives the best mode of practicing the invention now known to us, both so far as the method is concerned and for the manufacture of the best bars. However, it must be understood that resistor bars of different electrical properties and physical size are wanted and for many uses the less pure grades of silicon carbide and molybdenum silicide compounds may be used for impregnating the SiC not only to save expense but to obtain lower conductivity in the hot zones which in many cases is wanted. The less pure grades of silicon carbide give lower conductivity. The black variety which may be used to carry out our invention, in many cases analyzes as low as 90% silicon carbide.

It will thus be seen that we have provided by this invention electrical heater bars for electric furnaces and a method of producing them in which the various objects hereinabove set forth together with many thoroughly practical advantages are successfully achieved. As many possible embodiments may be made of the above invention and as many changes might be made in the embodiments above set forth, it is to be understood that all matter hereinbefore set forth or shown in the accompanying drawings is to be interpreted as illustrative and not in a limiting sense.

We claim:

1. Method of making a hot zone for an electrical resistance bar comprising forming a tube of recrystallized hexagonal silicon carbide, filling the tube with molybdenum silicide, and then heating the tube containing the molybdenum silicide under reducing conditions to a temperature between 2000° C. and 2600° C. then cutting the tube to form a helix therein.

2. Method of making an electric furnace bar having a hot zone between cold ends comprising forming a tube out of silicon carbide fines and a temporary binder; heating the tube to between 1650° C. and 2650° C. and thereby recrystallizing the silicon carbide; plugging one end of the tube with a refractory plug; filling the tube to the length of the cold end minus that of the plug and minus that of the portion of that cold end which might, under

the highest temperature conditions under which the bar is operated, be exposed to temperatures as high as 1000° C. with silicon; inserting a second refractory plug; filling the tube to the length of the hot zone plus those portions of the two cold ends of the bar which might be exposed to temperatures higher than 1000° C., with molybdenum silicide; inserting a third refractory plug; filling the tube to the remaining length thereof minus that of another plug with silicon; inserting another refractory plug in the end of the tube; heating the tube to a temperature of between 2000° C. and 2600° C. under reducing conditions thereby impregnating the ends with silicon and the middle with molybdenum silicide; and cutting a helix between the cold ends to form the hot zone.

3. Method according to claim 2 in which the silicon contains boron carbide in the amount of from 0.078% to 5% of the silicon content.

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