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AT ELEVATED TEMPERATURES

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2 Sheets-Sheet 1

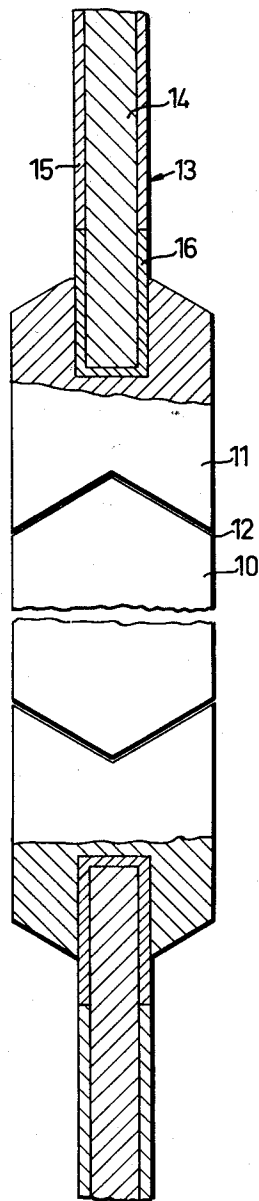


Fig. 1

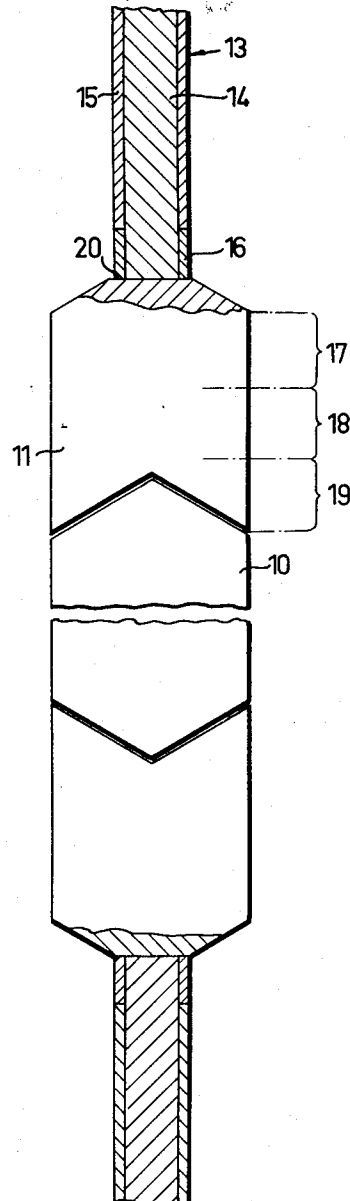


Fig. 1a

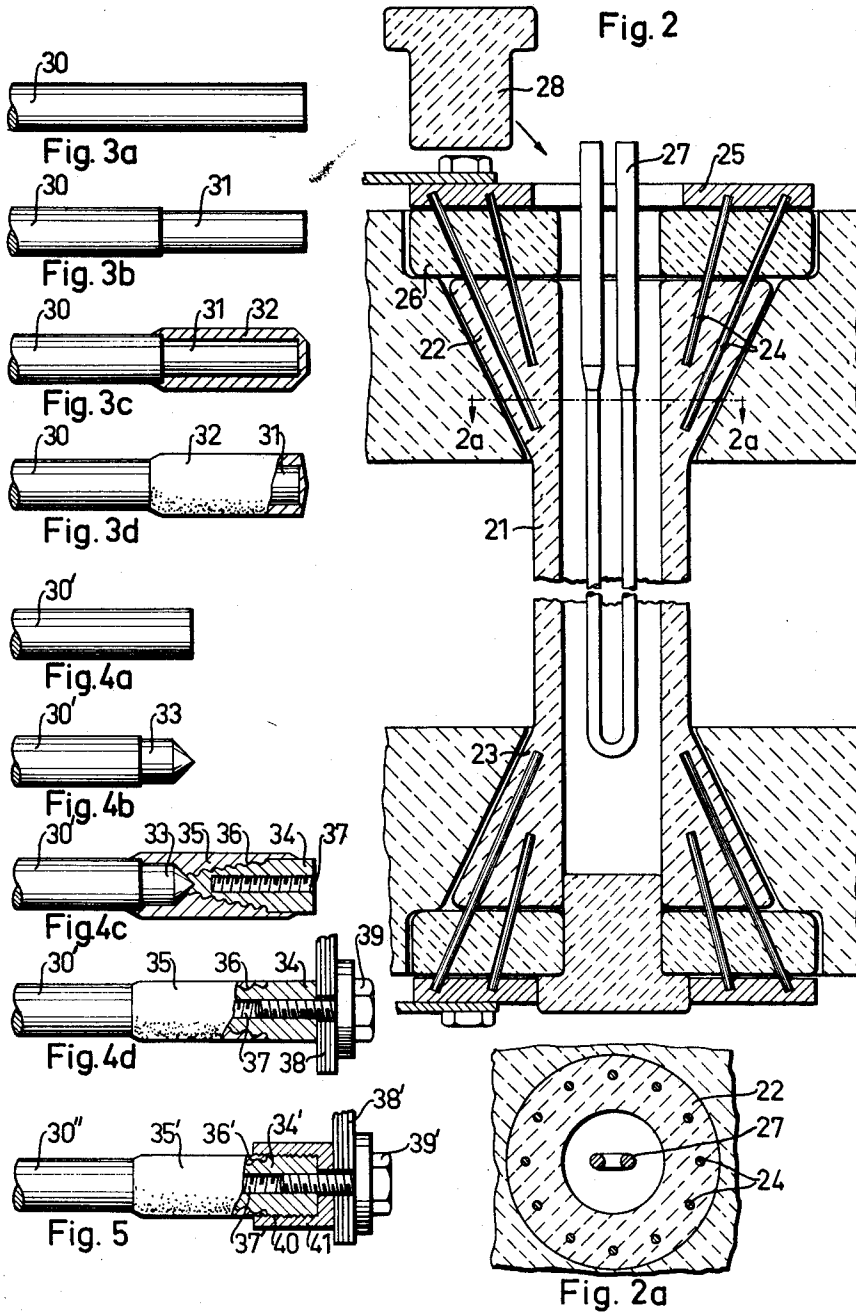
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**ELECTRICALLY CONDUCTIVE ELEMENT FOR
USE AT ELEVATED TEMPERATURES**

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8 Claims. (Cl. 338—322)

This invention relates to electrically conductive elements for use at elevated temperatures. Elements according to this invention may find various applications, such as for heating of furnaces, as tube type furnaces, as sources of radiation, and as thermo-couples wherein a hot junction is arranged within the element. However, as such elements are particularly well adapted for producing very high furnace temperatures they will be discussed herein with reference made to furnace elements as a non-limiting example.

It is already known that certain highly refractory oxides become electrically conductive at temperatures above about 900° C. Examples of such material are toria and zirconia either singly or in mixture with oxides of rare metals, such as yttria, ceria and lanthana. Furthermore it has been suggested to use such highly refractory oxides and oxide mixtures in the resistor proper of electrical resistance heating elements as well as to clamp such resistors between contact blocks. Thereby the dimensions and the composition of these contact blocks may be chosen to provide for such a temperature gradient across each contact block from the resistor to the lead-in electrodes that the latter is protected from the high temperatures which prevail in the resistor and which otherwise would cause the lead-in electrodes to fuse.

Although it is known that very high temperatures may be produced with the aid of electrical resistance heating elements of the class described, and although certain provisions have been made to prevent the lead-in electrodes from fusing, such elements have, however, as far as known not found any practical application.

The principal object of the present invention is to provide an electrically conductive element for use, in practice, at elevated temperatures in air, for example temperatures of up to 2200° C., and more.

According to the invention this object is realized with electrically conductive elements of the class described by employing as lead-in electrodes only those composed essentially of highly temperature resistant silicides. Examples of such silicides are silicides of molybdenum, titanium, tungsten, niobium or zirconium, either singly or in combination, and possibly with minor portions of other metallic or nonmetallic substances. The silicide content should be at least 30 percent by volume and is preferably 75 percent by volume, or more. Lead-in electrodes composed of molybdenum disilicide or containing molybdenum disilicide to an essential proportion have been found particularly advantageous. A particular advantage of employing molybdenum disilicide is to be found in that the strongly positive temperature coefficient of this material acts in a balancing sense with respect to the strongly negative temperature coefficient of the oxide resistor. This has a favourable effect on the operation characteristics and the usable life time of the element.

The lead-in electrodes may be insulated in a suitable manner. Preferably, however, oxides of the class which are electrically nonconducting at very high temperatures are used for the purpose. Examples of such oxides are

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baryllia and alumina, either singly or in combination. The insulating layer may be applied in any convenient manner such as by hot spraying or the like. The insulation may also consist of a tube such as of a ceramic material of the above mentioned class which tube is disposed to surround the lead-in electrode.

Of course, the electrically conductive element according to the invention may be constructed and designed in any suitable manner according to the particular field of use.

In one case, however, a resistance heating element according to the invention is made up in several parts, viz. the following parts: two straight rod or tube shaped lead-in electrodes of uniform cross-section, composed of molybdenum disilicide, MoSi₂, and as by flame spraying provided with an electrical insulation of one or more oxides which are nonconducting at very high temperatures, a resistor portion, composed of an oxide of the above mentioned behaviour or a mixture of such oxides, as for instance a mixture of thorium and ceria, and two contact blocks disposed between the resistor and said lead-in electrodes respectively, and between which the resistor is clamped.

The contact blocks have been provided in order to improve the electrical contact between the lead-in electrodes and the resistor proper, and preferably said contact blocks are composed of zirconia to an essential proportion. Preferably each lead-in electrode is let into a bore in its corresponding contact block. As is well known, however, there gradually develops a thin silicon oxide coating on the silicide lead-in electrode, and as this coating develops little by little there arises the danger of interruption of the current flow, due to the very high specific resistance of the coating layer. To avoid this drawback the silicide lead-in electrode according to the invention may be coated at the end portion thereof with a thin layer of fine grained zirconia, which thereafter, at elevated temperature in air, is flashed on to the silicon oxide coating and reacts therewith into zirconium silicate. Thereafter the end portion of the lead-in electrode thus prepared may be fitted to the contact block whereby a satisfying current transition has been secured.

According to the invention the contact blocks also may be formed by a powder-metallurgical process in a manner such that they each comprise two different portions, one portion which is composed essentially of zirconia or another oxide which is electrically conductive at elevated temperatures whereas the other portion is composed essentially of zirconia and an additive of the above mentioned kind, for instance molybdenum disilicide. Thereby, the lead-in electrode of molybdenum disilicide or a similar silicide is secured to the silicide containing portion of the contact block as by sintering. The contact blocks which have been formed by a powder-metallurgical process preferably should be subjected to a pre-oxidation, whereby the silicide particles are coated with a thin silicon oxide layer which reacts with the admixed zirconia into zirconium silicate. In order to prevent the development of insulating boundary layers the transition from the silicide rich to the oxide rich portion of the contact block is advantageously made diffuse or continuous along a certain length. It is possible, however, to give the electrically conductive element according to the invention the shape of a tube with enlarged end portions in each of which there are fitted several spaced silicide lead-in electrodes of reduced cross section.

Now it has been found difficult in certain cases to obtain satisfactory electrical connections with the terminal surfaces of the lead-in electrodes of the above mentioned kind. Such electrodes have very hard surfaces so that they exhibit substantially no deformation and terminals, such as clamping terminals, used thereon for

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connecting them to a source of electrical energy in certain cases have not been able to provide the desired intimate electrical contact with the entire surface area of the corresponding surfaces of the electrodes. Contact is made only by "spot contact" on localized areas greatly concentrating the current applied on these areas resulting in an unfavorable reaction between the materials of the connecting members and the lead-in electrode material and arcing as well as embrittlement of the lead-in electrodes material eventually resulting in the destruction of the connection.

While attempts have been made to solve the contact surface problem by accurately finishing the terminal surface of the lead-in electrodes still the service life of the lead-in electrode has remained greatly reduced. The matching of clamping terminals and the lead-in electrodes has not helped very much. Several materials, as for example, aluminium, steel, nickel and the like have been used for the clamping terminals, however, the aforementioned unfavorable reaction still takes place between these different materials and the lead-in electrode materials.

Bonding the terminal clamping members to the lead-in electrodes by the use of hard solders or welding them to the electrodes has not provided a solution to the problem since the deposition of the "weld" metals and the shrinking that takes place upon the cooling thereof results in the formation of internal stresses in the base material of the electrodes of such a magnitude that eventually fractures develop destroying the connection.

It is a secondary object of the invention to provide a lead-in electrode of the above discussed class wherein the just mentioned limitations are overcome.

A feature of the lead-in electrode in accordance with the invention is that an electrically conductive metallic coating is applied by flame spraying to the terminal portion thereof. When used for forming terminals for clamping terminals such coating is preferably built-up to a sufficient thickness for machining and then it is machined, for example by turning, to finish the surfaces thereof. The metallic coating is preferably a layer of aluminium or some similar material that is deformable and comparatively soft at room temperature and will thus provide contact over the entire surface of the contact area of the coating. In this manner a terminal zone is formed on the lead-in electrode that will provide intimate contact with clamping terminals and the like over the entire contact area thereof. The thickness of the finished metallic coating must be at least .2 mm., preferably greater than .5 mm. On the other hand, said thickness should preferably not exceed 3.0 mm.

The application of the coating or layer of aluminium by flame spraying precludes the generation of internal stresses in the base electrode material and eliminates the aforementioned unfavorable reaction causing embrittlement since the application of the coating material does not result in the high temperatures necessary for the deposition of "weld" metals thereby eliminating the possibility of rupture of the electrode material and the possible destruction of the terminal during service operation. Moreover, such coating makes it possible to connect one or more silicide lead-in electrodes to distribution bars or the like, for instance by flame spraying.

To start up a resistance heating element of this kind it is necessary to heat the resistor proper to about 900° C. Preferably this heating is performed by means of molybdenum disilicide elements. Such elements may either be stationary or adapted to be removed from the furnace as soon as the ceramic resistor proper has attained the necessary starting temperature at which it becomes conductive.

Hitherto, it has been considered necessary to control resistors of highly refractory oxides separately in order to avoid that the current—due to the highly negative temperature coefficient of such materials—channels down one resistor only which might lead to overheating. This

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serious limitation may be overcome according to the invention as the lead-in electrode material exhibits a very highly positive temperature coefficient. Thus, it may now be found possible to control several elements of the class discussed herein simultaneously. This necessitates, however, that the resistance of the lead-in electrodes corresponds, at least generally, to that of the oxide resistor proper.

Other objects, features and advantages of the invention will be understood from the following description and claims in conjunction with the accompanying drawings which illustrate by way of example some embodiments of the resistance heating element and the terminal connection, and in which

Fig. 1 is a fragmentary side view of a resistance heating element according to the invention;

Fig. 1a is a fragmentary side view of a slightly modified resistance heating element according to the invention and is similar to that in Fig. 1;

Fig. 2 is a fragmentary longitudinal axial section of second embodiment of a resistance heating element according to the invention installed in a furnace;

Fig. 2a is a cross section along line 2a—2a in Fig. 2;

Fig. 3a is a fragmentary side view of a lead-in electrode prior to forming thereon a terminal according to the invention; and

Fig. 3b is a fragmentary side view showing the end portion of the lead-in electrode in Fig. 3a after the diameter thereof is reduced in preparation for forming a terminal thereon; and

Fig. 3c is a fragmentary side view of a lead-in electrode with a terminal in accordance with the invention and is illustrative of the thickness to which the terminal is built up; and

Fig. 3d is a fragmentary side view of a lead-in electrode showing the terminal thereon partly in section and is illustrative of the finished surface of the contact area of the terminal according to the invention; and

Fig. 4a is a fragmentary side view of a lead-in electrode similar to Fig. 3a; and

Fig. 4b is a fragmentary side view showing the end portion of the lead-in electrode in Fig. 4a prepared for formation of a terminal thereon; and

Fig. 4c is a fragmentary side view of the lead-in electrode shown in Fig. 4b and is illustrative of a second embodiment of a terminal for lead-in electrodes according to the invention; and

Fig. 4d is a fragmentary side view partly in section of the lead-in electrode in Fig. 4c and is illustrative of an assembled terminal connection according to the invention; and

Fig. 5 is a fragmentary side view of a third embodiment of a terminal according to the present invention.

In Fig. 1 the reference 10 denotes the resistor proper of the element. This resistor 10 is composed, for instance, of thoria in mixture with a small amount of ceria. The reference 11 denotes a contact block of for instance zirconia or zirconia and molybdenum disilicide. The joint 12 between the resistor 10 and the contact block 11 is loose; i.e. arranged in such a manner that the components are held together only by a clamping action. In a bore in the contact block 11 there is introduced one end portion of a lead-in electrode 13. This consists of a straight rod 14 of molybdenum disilicide which is insulated by a coating 15 of for instance beryllia, preferably applied by spraying. The end portion of the lead-in electrode is provided with a gas tight glazing 16 of zirconium silicate.

In the embodiment as shown in Fig. 1a the contact block 10 is made by a powder metallurgical process and composed of molybdenum disilicide, portion 17, molybdenum disilicide in mixture with zirconia, portion 18, and zirconia, portion 19, in a continuously varying composition. In the portion 18 there also exists zirconium silicate, which has been developed at the preoxidation of

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the contact block. In this embodiment the lead-in electrode is connected to the contact block by means of a welded joint 20.

The resistor proper of the heating element in Figs. 2 and 2a is in the form of a tube 21 of thoria or zirconia, either singly or in combination with admixtures to small proportions. The end portions 22 and 23 of the tube shaped resistor 21 are enlarged so that a considerable cooling effect is obtained. In said end portions there are introduced the inner ends of several spaced lead-in electrodes 24 which are composed mainly of molybdenum disilicide and which are of a rather small cross sectional area. The lead-in electrodes 24 are disposed in a portion of the resistor body which in operation attains a temperature not exceeding 1700° C. but not below about 900° C. The other end of said lead-in electrodes protrude from the resistor tube 21 and are connected to a source of electric current by means of an annular plate 25 of, for instance, aluminium. Preferably, such protruding ends are provided with a flame sprayed coating of aluminium, and these ends may be connected to the annulus 25 by a further flame spraying operation. Such flame spraying is preferred for making this connection but it is, of course, also possible to introduce the aluminium flame sprayed terminal ends into bores in the annulus 25. The inner ends of the lead-in electrodes may be provided with a thin coating of zirconium silicate. Between the annular plate 25 and the end surface of the resistor tube 21 there is disposed a ceramic brick 26 of the kind which is electrically insulating at high temperatures, e.g. composed of Al_2O_3 or BeO . The advantage of using several molybdenum disilicide lead-in electrodes of reduced cross sectional area instead of single electrode is mainly to be found in that such electrodes make it possible to considerably reduce the thermal stresses between the metallic and the oxidic materials. Moreover, the danger of insufficient electrical contact between the metallic and the oxidic materials is considerably reduced in as much as the contact surface has been enlarged. Finally, the advantage of an even current supply is secured whereby the tendency for all of the current to channel down one side only of the resistor proper is considerably reduced.

The construction as shown in Figs. 2 and 2a makes it possible to start up the element in a very simple manner, i.e. to heat it to a temperature at which it becomes conductive. As illustrated such starting up is performed by introducing into the resistor tube 21 a resistance heating element 27, preferably essentially consisting of molybdenum disilicide and preferably having the shape of a hair-pin, and heating said element 27 to a high temperature. Thereby, the resistor tube 21 rapidly attains the necessary temperature of 900° C. or more. Of course, the starting element 27 is removed immediately as the resistor tube 21 starts up, whereafter an insulating plug 28 is inserted in place of the starting element to prevent losses.

With reference now to Figs. 3a-3d, 4a-4d, and Fig. 5, which illustrate preferred methods of forming terminals on lead-in electrodes of resistance heating elements of the class discussed above, particularly with reference to Figs. 1 and 1a, on the drawing, a lead-in electrode 30 made of molybdenum disilicide, or a similar material having a hard surface, and having any given diameter, for example 14 mm., is machined on a portion on which a terminal is to be formed, as for example, an end portion 31 to finish the surfaces thereof in preparation for forming a terminal on the end of the lead-in electrode.

The surfaces of the end portion may be prepared by roughening them by sand blasting or other means prior to forming a terminal thereon. A metallic, electrically conductive coating or covering layer 32 is then applied circumferentially around the end portion 31 and over the end of the lead-in electrode so that coat 32 extends the full length of portion 31. The coating 32 is applied by flame spraying on portion 31 a suitable conductive ma-

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terial which is relatively deformable at room temperature, as for example aluminium, silver, copper or some other material. The thickness of the coating 3 when applied must be sufficiently thick to permit finishing the surface thereof, as for example by machining it.

Lead-in electrodes formed in this manner are connected to a source of current, not shown, by connecting a lug or conductor thereto with a clamping terminal and a bolt assembly. The relatively soft or deformable coat provides intimate electrical contact between the corresponding surfaces of the lead-in electrode terminal and the clamping terminal when bolt is tightened.

Referring to the drawings (Figs. 4a-4d) a second embodiment of a terminal, according to the invention, is formed on a lead-in electrode 30' by matching an end portion 33 thereof and tapering the tip or end of the lead-in electrode in the manner shown in Fig. 4b. A connector element in the form of a plug 34 having an internally threaded central bore 37, as shown, (Fig. 4c) is placed and held in end-to-end relationship with the end portion 33 for fixed assembly with the resistor 30'. A coating of conductive metal 25 is then sprayed over the end portion 33 circumferentially around the plug 34 and in an axial direction thereof. The thickness of the coating 35 is such that the plug is well embedded therein.

The plug 34 may be made of aluminium or of some suitable material and is preferably provided with serrations or corrugations 36 on the tapered portion thereof in order to insure a greater bonding area between the plug 34 and the metallic coat 35.

The end of the plug meeting the tapered tip of the lead-in electrode is recessed to accept the tip of the lead-in electrode to allow ease of alignment of the members to be assembled and maintain them coaxial during assembly.

Subsequent to assembly coat 35 is preferably machined to finish dimensions. The finished lead-in electrode is connected to a current source, not shown, by clamping a lug terminal or conductor 38 across the end of the assembled plug with a threaded bolt 39, as shown.

Referring to Fig. 5 wherein is shown a third embodiment of the invention a plug connector 34' provided with corrugations 36' in the manner heretofore discussed with respect to the embodiment shown in Fig. 4c is assembled with the lead-in electrode 30'' by coating the plug connector and the lead-in electrode end portion to form a terminal in the manner heretofore discussed. In this instance, the connector element 34' is provided with an exterior thread 40 on which is threaded a conductive adapter 41 to which an electrically conductive lug or conductor 38' is connected by a threaded bolt 39' (in the same manner as shown in Fig. 4d). The adapter 41 provides additional contact surface between the plug connector 34' and element 38' thereby allowing maximum currents to be applied through the terminal.

In order to improve the bond between the metallic coat and the connector elements 34 and 34' the connectors are preferably sprayed with a thin metal coating of a suitable material, as for example, molybdenum, iron, stainless steel or zinc and the like before assembly in end-to-end relationship with the lead-in electrode 30.

In each of the embodiments of the invention the lead-in electrode 30 can be pre-glazed prior to forming the terminal portion therein in order to insure the serviceability of the lead-in electrode under all kinds of atmospheric conditions. Prior to machining, the material is heated, at a rapid rate to a high enough temperature, under oxidizing conditions to form the characteristic vitreous glaze of these materials. The glazing effectively seals the pores precluding the penetration of oxygen under service conditions thereby forming an effective anti-oxidation covering on the lead-in electrode. In order to improve the anti-oxidation cover glazing constituents or additives may be employed in the composition of the lead-in electrode material, as for example boric oxide (B_2O_3)

and silicates such as aluminium silicide or mullite ($3\text{AlO}_3\cdot 2\text{SiO}_2$), in suitable percentages. Moreover, an antioxidation cover can be formed by firing a high-temperature glass as borosilicate on the lead-in electrode material. The borosilicate preferably includes a fine grained heat resistant oxide such as chromium oxide (Cr_2O_3), dispersed therein.

While preferred embodiments of the invention have been illustrated and described, it will be understood that the invention is in no way limited to these embodiments and that many changes may be made within the spirit and scope of the invention as defined by the following claims:

What I claim and desire to secure by Letters Patent is:

1. An electrically conducting element for use at elevated temperatures, wherein the resistor proper is composed of a highly refractory oxide of the kind which becomes electrically conductive at temperatures above about 900°C ., and wherein the lead-in electrodes are composed at least to an essential proportion of a highly temperature resistant silicide, and are provided with an insulation of at least one oxide of the kind which is electrically non-conducting at very high temperatures.

2. An electrically conductive element for use at elevated temperatures comprising, a resistor of a highly refractory oxide of the kind which becomes electrically conductive at temperatures above about 900°C ., means for holding the resistor and providing electrical current thereto comprising, a lead-in electrode having a composition comprising silicides of the group consisting of molybdenum, titanium, tungsten, niobium and zirconium, and the silicide content of each lead-in electrode being at least 30 percent by volume of the composition of the lead-in electrode.

3. An electrically conductive element for use at elevated temperatures comprising, a resistor of a highly refractory oxide of the kind which becomes electrically conductive at temperatures above about 900°C . comprising oxides of the group thoria and zirconia, means for holding the resistor and providing electrical current thereto comprising, a lead-in electrode having a composition comprising silicides of the group consisting of molybdenum, titanium, tungsten, niobium and zirconium, and the silicide content of each lead-in electrode being at least 30 percent by volume of the composition of the lead-in electrode.

4. An electrically conductive element for use at elevated temperatures comprising, a resistor of a highly refractory oxide of the kind which becomes electrically conductive at temperatures about about 900°C . comprising oxides of the group thoria and zirconia, means for holding the resistor and providing electrical current thereto comprising, a lead-in electrode having a composition comprising silicides of the group consisting of molybdenum, titanium, tungsten, niobium and zirconium, the silicide content of each lead-in being at least 30 percent by volume of the composition of the lead-in electrode, and said lead-in electrode having a coating of zirconium silicate along a portion thereof in contact with said holding means.

5. An electrically conductive element for use at ele-

ated temperatures comprising, a resistor of a highly refractory oxide of the kind which becomes electrically conductive at temperatures above about 900°C ., electrically conductive contact blocks holding the resistor extending axially between them, lead-in electrodes electrically connected to respective blocks, each lead-in electrode comprising silicides of the group consisting of molybdenum, titanium, tungsten, niobium and zirconium and the silicide content of each lead-in electrode being at least 30 percent by volume of the lead-in electrode.

6. An electrically conductive element for use at elevated temperatures comprising, a resistor of a highly refractory oxide of the kind which becomes electrically conductive at temperatures above about 900°C . comprising oxides of the group thoria and zirconia, electrically conductive contact blocks holding the resistor extending axially between them, lead-in electrodes electrically connected to respective blocks, each lead-in electrode comprising silicides of the group consisting of molybdenum, titanium, tungsten, niobium and zirconium and the silicide content of each lead-in electrode being at least 30 percent by volume of the lead-in electrode.

7. An electrically conductive element for use at elevated temperatures comprising, a resistor of a highly refractory oxide of the kind which becomes electrically conductive at temperatures above about 900°C ., electrically conductive contact blocks holding the resistor extending axially between them, and comprising separate layers of the group molybdenum disilicide, a mixture of molybdenum disilicide and zirconia, and zirconia, lead-in electrodes electrically connected to respective blocks, each lead-in electrode comprising silicides of the group consisting of molybdenum, titanium, tungsten, niobium and zirconium and the silicide content of each lead-in electrode being at least 30 percent by volume of the lead-in electrode.

8. An electrically conductive element for use at elevated temperatures comprising, a resistor of a highly refractory oxide of the kind which becomes electrically conductive at temperatures above about 900°C . comprising oxides of the group consisting of thoria and zirconia, electrically conductive contact blocks holding the resistor extending axially between them and comprising in separate layers molybdenum disilicide, a mixture of molybdenum disilicide and zirconia, lead-in electrodes electrically connected to respective blocks, each lead-in electrode comprising silicides of the group consisting of molybdenum, titanium, tungsten, niobium and zirconium and the silicide content of each lead-in electrode being at least 30 percent by volume of the lead-in electrode.

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