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IMPREGNATED SILICON CARBIDE ARTICLE AND THE MANUFACTURE THEREOF

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Fig. 1.

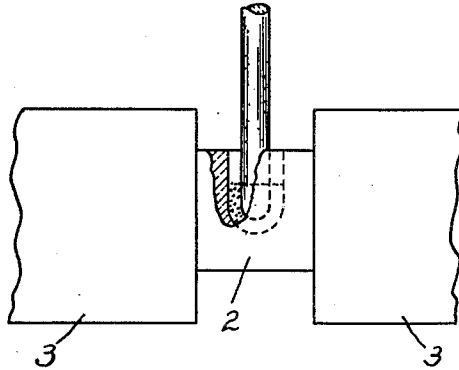


Fig. 2.

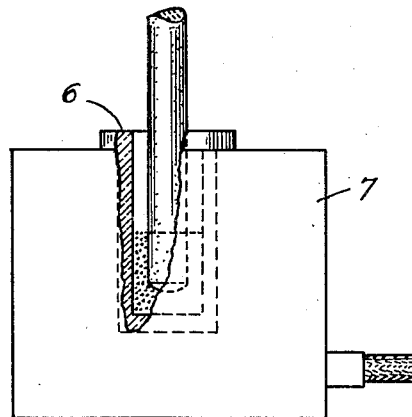


Fig. 3.



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IMPREGNATED SILICON CARBIDE ARTICLE AND THE MANUFACTURE THEREOF

Application filed November 17, 1931, Serial No. 575,578, and in Canada April 28, 1930.

This invention relates to non-metallic articles composed principally of silicon carbide, which are impregnated with a metal, or combination of metals, or with a material
5 such as silicon having metallic characteristics. The invention also relates to the treatment of silicon carbide resistors, and especially to the treatment of the terminal portions of such resistors to increase their electrical conductivity.

10 In the use of silicon carbide resistors for electrical heating purposes, one of the principal difficulties encountered is that of making satisfactory electrical contact. This is especially true of high temperature electric furnace elements, which often operate at temperatures as high as 1400 to 1500° C. If the metal terminal is brought into direct contact with the silicon carbide at these temperatures, the excessive heating of the terminal
15 metal and the oxidation of the end portion of the rod due to local overheating and arcing at the points of contact soon cause the electrical connection to become insulating and the metal terminal is often completely disintegrated.

20 Various efforts have been made to increase the electrical conductivity of the terminal portions of the resistor so as to afford a lower operating temperature at the contact. Although the methods heretofore used have been moderately successful for the smaller elements operating at comparatively low temperatures, they have not proved entirely
25 satisfactory for the larger elements operating in high temperature electric furnaces, because they have not afforded a terminal portion of considerable length and uniformly low electrical conductivity throughout the
30 entire cross section of the element.

In my process I impregnate the entire end portion of the resistor with molten metal so as to produce a dense substantially impermeable end of high electrical conductivity.
35 The end of the rod after treatment is uniformly metallized throughout its cross section, and the length of the treated portion can be readily controlled. By a further treatment of the impregnated portion of the resistor after impregnation is complete, I have

found it possible to produce an end of even lower electrical resistance than one in which the impregnating material merely fills the pores of the silicon carbide.

The complete impregnation of the terminal
40 portion of a silicon carbide resistor with molten metal has heretofore been considered impractical because of the difficulty in causing the metal to flow into the pores of the article. It is well known that molten metals, even when heated considerably above their
45 melting points, will not wet nor permeate non-metallic objects, owing to the high surface tension of the metal. Silicon, which I have found to be the most suitable material for
50 impregnation of the ends of the resistor, offers even greater difficulties than most of the common metals when used as a molten impregnating material. Silicon melts at approximately 1450° C. and even when heated to
55 approximately 1700° C. it will not permeate the end of the resistor. At this temperature any silicon which may adhere to the element is merely in the form of a surface crust. If the silicon is heated to a higher temperature
60 as for example about 2000° C. and the element immersed in the molten bath, a vigorous reaction seems to take place, and the greater part of the immersed rod is disrupted. Even when the immersed portion can be recovered intact,
65 the junction between the body of the rod and the portion immersed is so weak mechanically that the element is not suitable for commercial use.

Another difficulty arises from the extreme
70 reactivity of the silicon. It is almost impossible to maintain a silicon bath suitable for impregnation for any prolonged period of time, for the only practicable container is carbon, and the silicon oxidizes rapidly if
75 exposed to the air and is converted to silicon carbide if covered or protected. This is especially true when small quantities of silicon are used.

80 Immersing of the end of the resistor in other molten metals at any ordinary temperature such as would be used for pouring or casting does not result in the impregnation of the terminal portion of the rod.

I have found that silicon and most of the 100

common metals will completely impregnate silicon carbide bodies if the temperature is raised above a definite critical value, which will vary somewhat with the metal used, but is comparatively high, and may be as high as 2000° C. Aluminum, nickel, cobalt and chromium, as well as silicon, will flow into the pores of a previously formed silicon carbide article at temperatures of approximately 2000° C., and will permeate it throughout its entire cross section. When the critical temperature is reached the impregnation is almost instantaneous, and I have found that there is sufficient capillary attraction between the silicon carbide and the metal at these temperatures that the molten metal will be absorbed throughout the silicon carbide body even when the metal is present in only a very small excess over that necessary to impregnate the immersed portion. Because of the great reduction in interfacial tension between the silicon carbide and the impregnating material at the critical temperature, I am able to heat together the end of the rod and a small excess of the impregnating material until the critical temperature is reached, whereupon a considerable proportion of the total amount of metal used is absorbed into the rod.

By heating the impregnating material and the end of the resistor together in this manner from a comparatively low temperature, I am able to secure an end which is completely impregnated throughout its cross section without the disruption and mechanical weakening which occur with the usual dipping process. By further heating to a higher temperature I am able to remove by vaporization the small excess of impregnating material not absorbed into the rod, so that the original contour of the element is retained without any crust or globules of excess metal adhering to the surface of the element.

Upon still further heating of the end of the element to a very high temperature after the excess metal is removed, I have found that the character and structure of the impregnated material changes and that a still greater decrease in electrical resistance results.

A method of carrying out my invention and a type of end made possible by certain modifications in the process are shown in the accompanying drawing.

In the drawing:

Figure 1 is a diagrammatic view showing a silicon carbide resistor positioned in a type of crucible suitable for impregnation and surrounded by granular impregnating material;

Figure 2 represents a deeper crucible than that shown in Figure 1, the crucible being removable from the high temperature source of heat;

Figure 3 is a sectional view showing an impregnated resistor in which the junction between the impregnated and unimpregnated

portions presents a conical rather than a plane surface.

The resistors treated can be of the type commonly known and sold under the trade name of "Global", although other types of silicon carbide resistors can also be used. The "Global" resistors are self-bonded by a process of recrystallization, and I have found that the previously recrystallized material is readily impregnated and gives an end of high electrical conductivity without being weakened at the juncture between the impregnated and non-impregnated portions. The recrystallized material does not contain a bond which is fusible at the temperature of impregnation, and it retains its strength up to very high temperatures, so that during the impregnation process there is no difficulty from the material losing its shape.

The impregnating material which I prefer to use is silicon or an alloy of silicon, because of the toughness and resistance to oxidation of the resulting product. In the case of silicon the critical impregnation temperature is approximately 1900° C., although it should be realized that the exact measurement of the critical temperature is difficult because of the fumes evolved in the process.

The use of silicon for impregnation possesses a number of advantages in comparison with most of the common metals. The siliconized end produced by my process is very tough, and being non-porous it can be operated at temperatures up to 1400° C. or even higher, with only a surface oxidation and with very little change in electrical resistance.

In carrying out my process, the resistor can be immersed in a slight excess of the impregnating material at a temperature only slightly above the melting point of the latter, and the end of the resistor and the surrounding material heated together to the critical temperature. With the higher melting metals, and especially with silicon, I have found, however, that a much stronger end can be produced by positioning the resistor in a crucible and surrounding it with the impregnating material in solid, and preferably in granular form. The crucible is then heated rapidly through the melting point of the impregnating material to the critical temperature, at which temperature the metal is absorbed into the rod almost instantaneously. The residual amount of the impregnating material left in the crucible or adhering to the rod can then be removed by vaporization. I have found that the crucible can be heated to temperatures of from 2500 to 2800° C. for a very short interval without decomposing the end of the silicon carbide rod, and that this temperature is sufficient to vaporize silicon, as well as most of the common metals and alloys.

One method of carrying out my invention is illustrated diagrammatically in Figure 1. The crucible 2 is preferably a carbon block,

which is adapted to be heated almost instantaneously to very high temperatures, as for example, by resistance heating using a very heavy current. The capacity of the crucible is only slightly greater than the volume of the end portion of the resistor to be immersed therein. The electrodes 3 can be of graphite in order to decrease their electrical resistance over that of the block used as a crucible, and by making the electrodes of sufficient size it is possible to conduct a current of from 10,000 to 20,000 amperes through the crucible if desired. The resistor 4 or its end portion is preferably preheated before positioning it in the crucible. Preheating is especially desirable with elements of large diameter in order to reduce thermal shock, but it is not absolutely necessary in all cases. After positioning the end of the resistor in the crucible, the end is surrounded with a predetermined quantity of impregnating material, preferably silicon or an alloy of silicon, the amount added being only slightly in excess of that necessary to impregnate the resistor to the desired length.

I shall describe the heating process as adapted for impregnation with silicon, although it will be realized that various modifications can be made, especially in the case of other impregnating materials. With silicon the heating should be comparatively rapid, owing to the tendency of the material to oxidize, vaporize and form silicon carbide by reaction with the carbon crucible before impregnation takes place.

It is very difficult to melt a small quantity of silicon in a carbon crucible and subsequently immerse the end of the resistor in the melt because of the extreme reactivity of the silicon and I have found that by surrounding the end of the rod with solid silicon and rapidly heating the crucible to the impregnation temperature, the silicon is absorbed into the rod, and the absorption is so nearly instantaneous that there is practically no difficulty from contamination of the silicon with oxide or silicon carbide before impregnation takes place.

The crucible and its contents, as illustrated in Figure 1, are heated rapidly until the excess metal is removed from the crucible by vaporization. The crucible and the end of the rod are still further heated for a very short interval, as for example, from 5 to 30 seconds, depending upon the rate at which heat is applied, in order to produce a further decrease in electrical resistance of the impregnated material. The final crucible temperature, as nearly as can be measured, is from 2500 to 2800° C., and care must be taken during the final heating period to control the process so as not to completely decompose the end of the rod to form graphite. The entire heating period can be from one to five minutes, and should not be extended

over a period greatly exceeding ten minutes. This extremely rapid heating can be effected either by passing a heavy current directly through the crucible, or by inserting a removable crucible into a previously heated high temperature furnace, as indicated by Figure 2 in which the removable crucible is inserted in a furnace 7, the furnace being represented conventionally. High frequency induction can also be used for rapid heating if desired.

By conducting the final vaporizing process while the element is positioned in the crucible, the crucible can be boiled completely dry, and the rod upon removal possesses a contour identical with that of the original element before treatment. If the element is removed after heating to about 1900 to 2000° C. impregnation is complete, but sufficient excess silicon usually adheres to the rod so as to give it a somewhat irregular contour and an unsightly appearance.

The additional heating of the resistor to a very high temperature after impregnation is complete produces a marked increase in electrical conductivity of the impregnated portion of the rod. For example, with a silicon carbide body having an original specific resistance of about 0.4 ohm per centimeter cube at the operating temperature of the resistor, the impregnated end before the high temperature treatment will have a specific resistance of .02 to .03 ohm per centimeter cube at the operating temperature of the resistor, whereas after high temperature heating this value can be reduced to approximately .01 ohm per centimeter cube. I believe this change is due to further alloying action between the silicon and the silicon carbide, and possibly to a partial decomposition of the silicon carbide into silicon and graphite. Under the microscope the silicon in the pores of the article seems to dissolve the smaller particles of the silicon carbide and also the surface of the larger particles, and the further the heating process is continued, the nearer the product resembles a true alloy instead of an aggregate in which the silicon merely fills the pores. As the decomposition temperature of the silicon carbide is approached or possibly slightly exceeded, the end becomes darker in color, and I believe that this material contains some graphite either in solid solution or otherwise alloyed with the silicon or the silicon carbide. Although the end may be partially decomposed it is still very resistant to oxidation, and at the same time it possesses a very high electrical conductivity. I have found that this material will retain its high conductivity and afford a very satisfactory "cold end" throughout the life of the element.

The alloying or solvent action of molten silicon on silicon carbide is further evidenced by the vigorous reaction and disruption of

the end of the rod when it is dipped into molten silicon at very high temperatures. With a large excess of silicon, such an action may cause a weakening of the bond between the individual grains so as to cause a partial dissolution or disruption of the article. In my process any alloying or solvent action takes place in situ after the silicon has been absorbed into the rod.

Although in carrying out my process the heating may be effected very rapidly, there is no abrupt change in the temperature gradient at any one point, as is the case if an attempt be made to dip the silicon carbide rod into a superheated bath of molten silicon, which causes a very abrupt change in the temperature gradient of the rod at the level of the molten bath. By my process I am able to obtain a high degree of mechanical strength at the junction between the impregnated and unimpregnated portions of the rod. This junction is the chief source of difficulty with an end of this type, and by certain modifications in the process I am able to still further improve the mechanical properties of the treated resistor.

In the case of silicon the addition of aluminum, preferably in quantities of from approximately 2 to 20 per cent, increases the toughness of the junction and minimizes breakage at this point. The addition of aluminum as an alloying ingredient to the silicon also seems to lower the temperature of final heating necessary to produce the high conductivity end, and if a partially decomposed end is desired, the process need not be subject to as accurate control to prevent complete decomposition of the end of the rod as is the case when silicon alone is used as the impregnating material, and the end of the rod heated to a higher temperature.

The tendency to fracture at the junction between the impregnated and unimpregnated portions can also be minimized by changing the shape of the junction so that it does not present a plane surface. The usual juncture is flat, and represents approximately the level of the impregnating liquid. By using a comparatively deep crucible, as shown in Figure 2, so that the element itself becomes heated above the critical impregnation temperature for a considerable distance beyond the level of the liquid, the impregnating material rises to a higher level in the central portion of the rod than near the outer surface, so that the juncture is approximately cone shaped, as indicated in Figure 3. Such a juncture is not only less readily fractured than the usual plane surface, but it offers a more gradual temperature gradient between the treated and the untreated portions during the operation of the element. The soaking up of the impregnating material to a higher level also lessens the excess to be removed by vaporization.

One of the characteristics of the material impregnated by my process is that it may be rendered completely impermeable to gases. The pores of the article can be filled completely with molten metal, which is not the case when the metal is incorporated into the original mix. When measured by the usual methods of determining the gas permeability of refractories, the gas permeability of my material is zero, whereas the usual recrystallized silicon carbide shows a very high permeability when subjected to such a test. A method of measuring the gas permeability of refractories, together with the experimental determination of the permeability of recrystallized silicon carbide, is given in the Bulletin of the University of Illinois, volume 23, No. 50, August 17, 1926, (Circular No. 14, engineering experiment station).

With a solid material oxidation is limited to the outer surface, whereas with the porous material resulting from the incorporation of the metal into the original mix, the metal is rapidly oxidized throughout the body of the article.

My method of impregnation affords a means for producing a silicon carbide body in which the pores are completely filled with metal, but in which the original shape of the article is retained. It is possible to obtain a very smooth surface after impregnation, especially when the body is composed of fine grit silicon carbide. For this reason my process is very advantageous for the impregnation of entire shapes of silicon carbide when the preservation of shape and surface is important, as is the case with bricks and other articles which must be made to size.

It is thus possible to obtain a non-porous refractory article of accurately controlled shape which possesses very high thermal and electrical conductivity. In carrying out such a process it is desirable to recrystallize the silicon carbide before impregnation by heating the article in a non-oxidizing atmosphere to a very high temperature at which the individual crystals grow together or become self-bonded. The formed article is then surrounded with a small excess of the impregnating material, heated to the critical temperature necessary for rapid impregnation, and the excess of the impregnating material then removed by vaporization.

By the term "metal" in the present specification and claims, I mean both the elements classified chemically as metals, and also the so-called "metalloids" such as silicon, which are commercially designated as metals and are commonly used as such for alloying purposes.

This application is a continuation-in-part of my earlier filed application Serial No. 382,004, filed July 29, 1929.

I claim:

1. The method of impregnating a silicon

carbide article with metal, which comprises surrounding the article with metal at a temperature substantially below the temperature of rapid impregnation of the metal into the article, and heating the article in contact with the surrounding metal to a temperature sufficient to cause a rapid flow of molten metal throughout the pores of the article.

2. The method of impregnating a silicon carbide article with metal, which comprises surrounding the article with a small excess of metal over the amount necessary to impregnate the article, the surrounding metal being at a temperature substantially below the temperature of rapid impregnation of the metal into the pores of the article, and heating the article in contact with the surrounding metal to a temperature sufficient to cause the greater portion of the metal surrounding the article to flow rapidly into the pores of the article and completely permeate the said article.

3. The method of impregnating a silicon carbide article with metal which comprises surrounding the article with a small excess of metal over the amount necessary to impregnate the article, the surrounding metal being at a temperature substantially below the temperature of rapid impregnation of the metal into the article, heating the article and the surrounding metal to a temperature at which the metal in the molten state flows rapidly into the pores of the article, and further heating the article until the excess metal is removed by vaporization.

4. The method of impregnating a silicon carbide body with metal which comprises surrounding the article with solid metal in excess of the amount necessary to impregnate the article, heating the surrounding metal in contact with the article to a temperature sufficient to liquefy the said metal and cause it to flow rapidly into the pores of the article, and further heating the article until the excess metal is removed by vaporization.

5. The method of making a shaped body of siliconized silicon carbide which comprises surrounding a previously formed silicon carbide article with solid silicon, and heating the article and the surrounding silicon to a temperature above approximately 1900° C.

6. The method of making a shaped body of siliconized silicon carbide which comprises surrounding a previously formed silicon carbide article with a small excess of solid silicon over the amount necessary to completely impregnate the article, heating the article and the surrounding silicon until the silicon in a molten state rapidly permeates the pores of the article, and further heating the article until the excess silicon is vaporized and the contour of the original shaped article is restored.

7. The method of increasing the electrical conductivity of the terminal portions of a

silicon carbide resistor, which comprises surrounding the end portion of the resistor with metal while the metal is at a temperature substantially below the temperature of rapid impregnation of the metal into the pores of the resistor, and heating the resistor and the surrounding metal until the metal in a molten condition completely permeates the end portion of the resistor throughout its entire cross section.

8. The method of increasing the electrical conductivity of the terminal portion of a silicon carbide resistor, which comprises surrounding the end portion of the resistor with solid silicon and rapidly heating the end of the resistor and the surrounding silicon to a temperature above approximately 1900° C.

9. The method of increasing the electrical conductivity of the terminal portion of a silicon carbide resistor which comprises surrounding the terminal portion of the resistor with a small excess of solid silicon over that necessary to impregnate the end of the resistor to a predetermined length and rapidly heating the resistor in contact with the silicon to a temperature of approximately 2500 to 2800° C.

10. The process described in claim 9 in which the period of heating is limited to less than ten minutes.

11. The method of increasing the electrical conductivity of the terminal portion of a silicon carbide resistor which comprises surrounding the end of the resistor with silicon at a temperature substantially below the temperature of rapid impregnation of silicon into a porous silicon carbide body, heating the end of the resistor and the surrounding silicon until the silicon in a molten condition flows into the pores of the end portion of the resistor, removing the excess silicon by vaporization, and further heating the resistor after the excess silicon has been driven off.

12. In the impregnation of silicon carbide with a molten impregnating material consisting substantially of silicon, the step comprising adding a minor proportion of aluminum to the silicon.

13. The method of increasing the electrical conductivity of the terminal portion of a silicon carbide resistor which comprises surrounding the end of the resistor with solid metal, and rapidly heating the end of the resistor and the surrounding metal to a very high temperature until incipient decomposition of the silicon carbide contained in the end portion of the resistor takes place.

14. The method of increasing the electrical conductivity of the terminal portion of a silicon carbide resistor which comprises surrounding the end of the resistor with solid silicon, and rapidly heating the end of the resistor and the surrounding silicon to a very high temperature until incipient decomposition

tion of the silicon carbide contained in the end portion of the resistor takes place.

15 15. A silicon carbide resistor having terminal portions impregnated with aluminum silicon alloy.

16. A silicon carbide resistor having terminal portions impregnated with metal, the juncture between the impregnated and the unimpregnated portions of the resistor being
10 substantially cone shaped.

17. A silicon carbide resistor having terminal portions impregnated with silicon, the juncture between the impregnated and unimpregnated portions being substantially cone
15 shaped.

18. A silicon carbide resistor having terminal portions impregnated with a material consisting substantially of silicon, the length of the impregnated portion being greater in
20 the inner portions of the resistor than at the surface of the resistor.

In testimony whereof, I have hereunto set my hand.

ALBERT H. HEYROTH.

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