

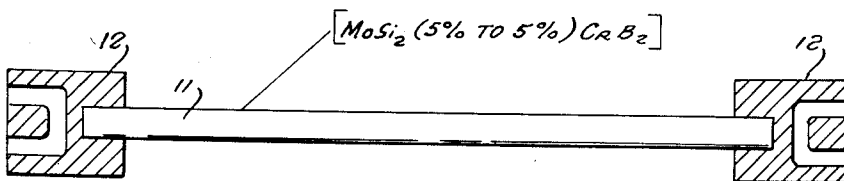
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HEATER BODIES AND THEIR PRODUCTION

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HEATER BODIES AND THEIR PRODUCTION

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This invention relates to electric resistor heater bodies, and more particularly to such bodies which are formed with molybdenum disilicide and to the production of such heater bodies.

It has long been known that molybdenum disilicide MoSi₂ has unusually desirable properties which would make it an ideal material for electric resistor heater bodies.

However, in the past, electrical heater rod bodies for electric furnaces and the like have in the past been made substantially out of silicon carbide, such heater bodies being known commercially as Globar bodies. The known silicon carbide heater bodies have a maximum operating temperature of about 1400° C., and they are made with a resistivity of 2000 to 5000 microhm centimeters because with lower resistivity it is difficult to supply such heater bodies with the much larger currents that would be required to bring them to the desired high operating temperatures.

Because of its relatively low electrical resistivity of about 22 microhm centimeters at room temperatures, no practical way was found in the past for utilizing molybdenum disilicide as electrical heater bodies. Cemented bodies of molybdenum disilicide are very brittle and fragile and proposals to increase the resistivity of molybdenum disilicide by additions of molybdenum aluminides, and/or high melting oxides, such as zirconium oxide, thorium oxide, which become conducting at high temperatures, and/or other high melting oxides, such as aluminum oxide, beryllium oxide, silicon oxide, likewise failed because these additions result in a further increase in the objectionable brittleness of molybdenum disilicide.

One phase of the present invention is based on the discovery that by combining molybdenum disilicide with chromium boride CrB₂, there is obtained a material of considerably smaller resistivity than molybdenum disilicide, the new material being also of a lower order of brittleness than molybdenum disilicide.

The foregoing and other objects of the invention will be best understood from the following description of exemplifications thereof, reference being made to the accompanying drawings, wherein the single figure is an elevational view with parts in section showing one form of heater body exemplifying the invention.

Bodies of pure molybdenum disilicide MoSi₂ which melts at about 1880° C. can be readily molded from MoSi₂ powders by powder metallurgy and ceramic techniques. Because of their high stability and resistance to corrosion in oxidizing atmospheres at 1700 to 1800° C., many proposals have been made in the past for using cemented MoSi₂ material in electric resistance heaters for operation at heating temperatures of about 1700° C. However, because MoSi₂ has a relatively low electrical resistivity of only 22 microhm centimeters at room temperature, heater bodies of this material would have to be made with a very thin cross-section, such as thin tubing or ribbon.

In addition, such cemented MoSi₂ material is very brittle and accordingly, thin heater bodies of such material are

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also impractical because of their excessive critical brittleness.

One phase of the invention is the discovery that superior electric heater bodies of similar physical characteristics as MoSi₂, but about 10 times higher resistivity will be obtained by combining molybdenum disilicide with chromium boride CrB₂ in a critical range of proportions and that such combined new material is of a lower order of brittleness than any other combination of molybdenum disilicide with other additional ingredients that might reduce the electrical conductivity thereof, including additions of the oxides, nitrides, silicides or other borides of the transition metals of the fourth, fifth and sixth groups of the periodic table.

An investigation has shown that MoSi₂ and chromium boride are mutually soluble over the range containing 5% to about 50% CrB₂ and that by combining MoSi₂ with 5% to 50% CrB₂, there is obtained a heater resistance material of a lower order of resistivity without increasing the brittleness of the material compared to MoSi₂. (Throughout the specification and claims, all proportions are given by weight, unless otherwise stated.) Superior results are obtained by combining 5% to 50% CrB₂ with MoSi₂. Within this critical range of proportions the stability of either of the components MoSi₂ and CrB₂ is not affected by any side reaction and the combined material may be readily produced in a well controlled manner.

As distinguished therefrom, if molybdenum disilicide is combined with other metal borides or with the oxides, nitrides and/or silicides of the metals of the fourth, fifth and sixth groups of the periodic table, the resulting materials are of such high brittleness as to render them utterly impractical for use in electrical heater bodies.

Investigations have shown that electrical resistivity of MoSi₂ at room temperature, increases from 22 microhm centimeters to about 200 microhm centimeters, or by a factor of 10, as the content of CrB₂ is increased from 0 to 5%, and that throughout this range, the MoSi₂ and CrB₂ form a series of solid solutions which exhibit metallic characteristics.

If the content of CrB₂ is increased above 50%, the resistivity of the resulting material decreases. On the other hand, if the molybdenum disilicide is combined with other elements for decreasing its resistivity, side reaction takes place which lead to the decomposition of the molybdenum disilicide compound. By way of example, if aluminum oxide Al₂O₃ is added to MoSi₂ and heated with it to elevated temperatures, side reaction takes place leading to the decomposition of the molybdenum disilicide into Mo—Al—Si—O type compounds wherein the Si—O phase is the most stable. The strength of such other body aggregate decreases from the original strength of pure molybdenum disilicide. Thus, whereas, pure MoSi₂ has a transverse rupture strength of 60,000 p. s. i. (pounds per square inch) when it is combined with aluminum oxide, its transverse rupture strength decreases to about 13,000 to 15,000 p. s. i. Furthermore, the equilibrium conditions for such aggregate can never be achieved, and the value of the transverse rupture strength is in a continuous flux.

An outstanding advantage of bodies of the invention which combine MoSi₂ with 5% up to 50% CrB₂ is the fact that such combined solid solution body exhibits essentially the structure of the CrB₂ compound. This factor is of great advantage since at elevated temperature, the temperature coefficient of resistivity of the MoSi₂ increases linearly with temperature. On the other hand, MoSi₂, if alloyed or combined in accordance with the invention with CrB₂ over the range of the proportions up to 50% CrB₂, gives a body with a temperature coefficient of resistance which approaches 0 at about 1200° C. and does not change with a further increase of the temperature up to about 1700 to 1900° C., the new material melting only at about

2000° C.. The negligible change in the resistivity of the combined material of the invention over the temperature range from about 1200 to 1900° C. and higher, is of great practical importance for electric heater bodies formed of such material.

By way of example, there will now be described one satisfactory procedure for producing such body of the invention. A powder mixture containing 10% CrB₂ with 90% MoSi₂ is hot pressed at 1500° C. into a cylindrical compact. The compact is then heated in hydrogen for 15 hours at 1300° C. and thereafter comminuted, yielding powder particles which contain the desired proportions of CrB₂ and MoSi₂ in completely alloyed solid solution form.

The alloy powder particles so obtained are then ready for forming heater bodies. To this end, the alloy powder particles may be cold pressed into the desired shape, pre-sintered, then further shaped to give it final shape, followed by sintering into the desired shaped heater body, such as a heater rod. The alloy powder may be also shaped into the desired heater body by extruding it after first mixing it with an extrusion vehicle such as methyl cellulose, followed by a sintering in vacuum. When making the desired heater body by the extrusion process, the extruded rods should be sintered while they are suspended in a hanging position to avoid distortion.

In producing out of the alloy powder the desired heater bodies by extrusion, it is important that the heating cycle of the sintering operation should be very rapid. In other words, the final sintering temperatures should be reached from room temperature within about 10 minutes. If the heating cycle is slow, the organic binder which is mixed with the alloy powder for carrying on the extrusion, will depart rapidly, leaving a relatively weak porous structure, thus endangering the production of satisfactory heater rod bodies. It is also important that the extrusion vehicle, such as methyl cellulose, should be de-aired before mixing it with the alloy powder, as the entrapped air interferes with the rapid heating of the rods and also causes blowups. In lieu of the methyl cellulose, other binders may be used such as ethyl cellulose, cellulose acetate with appropriate solvents.

The single figure indicates schematically the body exemplifying the invention. An elongated cylinder of MoSi₂ combined with 40% CrB₂ forms the heater body 11 which is provided at its ends with water-cooled electrode terminals 12.

Inasmuch as the addition of 5 to 50% of CrB₂ to MoSi₂ increases the resistivity of the resulting combined material only by a factor of 10, it is desirable to form heater bodies made of such material of only thin cross-section so that no excessively large currents be required for bringing the heater body material to the operating temperature of about 1700° C. According to the invention, desired heater

bodies having such thin heater body layer of MoSi₂ containing 10 to 50% CrB₂ are made as follows: A relatively rigid supporting body, such as a rod of ceramic material is covered with a surface layer of allowed powder particles of MoSi₂ containing in solid solution 5 to 50% CrB₂. The material for the applied coating layer may be prepared by mixing the alloy powder with a suspension medium such as methyl cellulose and the powder mixture so prepared is then applied as a uniform coating layer to the ceramic rod. The coated ceramic rod is then sintered at elevated temperature to solidify the applied coating layer and drive off the methyl cellulose in the manner analogous to that described above is preparing heater rods by extrusion.

Heaters of the invention formed in the manner described above, are superior to conventional silicon carbide heaters because they may be operated for prolonged periods of time without corrosion at temperatures much higher than the maximum temperature of 1400° at which such silicon carbide heaters may be used, the heaters of the invention cost only a fraction of the cost of such silicon carbide heaters.

The features and principles underlying the invention described above in connection with specific exemplifications, will suggest to those skilled in the art many other modifications thereof. It is accordingly desired that the appended claims be construed broadly and that they shall not be limited to the specific details shown and described in connection with exemplifications thereof.

I claim:

1. In an electric heater device, a heater resistor body having spaced metallic electrodes for passing heating current therethrough, said body consisting essentially of molybdenum disilicide MoSi₂ containing 5% to 50% CrB₂ in solid solution.

2. A heater device as claimed in claim 1, the molybdenum disilicide MoSi₂ of said body containing 10% to 50% CrB₂ and having a negligibly low thermal coefficient of resistivity at temperatures between about 1300 to 1700° C.

3. A heater device as claimed in claim 1, the molybdenum disilicide MoSi₂ of said body containing 40% to 50% CrB₂ and having a negligibly low thermal coefficient of resistivity at temperatures between about 1300 to 1700° C.

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