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L. W. COFFER

2,622,304

REFRACTORY

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Fig. 1

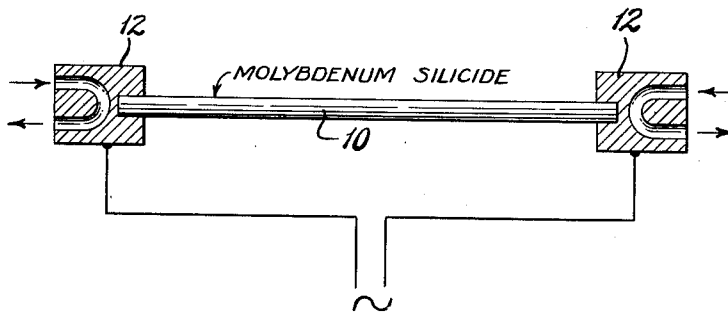
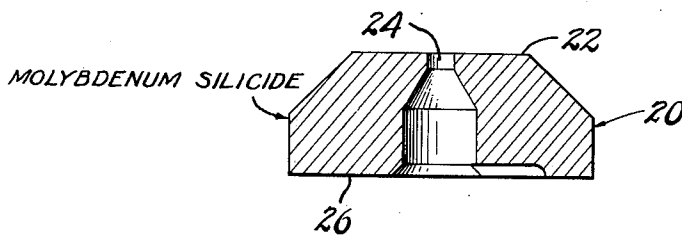


Fig. 2



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REFRACTORY

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1 Claim. (Cl. 25—156)

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The present invention relates to novel and improved refractory articles for use at high temperatures and to a novel and improved process of producing such articles.

Objects and advantages of the invention will be set forth in part hereinafter and in part will be obvious herefrom, or may be learned by practice with the invention, the same being realized and attained by means of the processes, steps, instrumentalities and combinations pointed out in the appended claim.

The invention consists in the novel steps, processes, parts, constructions, arrangements, combinations and improvements herein shown and described.

The accompanying drawings, referred to herein and constituting a part hereof, illustrate refractory articles in accordance with this invention and as produced by the process of the invention, and together with the description, serve to explain the principles of the invention.

Of the drawings:

Figure 1 is a schematic side elevation showing a typical and illustrative resistance heating element in accordance with the present invention; and

Figure 2 is a vertical sectional view.

The present invention has for its object the provision of a novel and improved process of forming and producing refractory bodies from powdered molybdenum silicide for use at relatively high temperatures under oxidizing as well as other conditions. A further object is the provision of novel and improved refractory articles for varied uses and which will withstand oxidation at high temperatures and are not seriously eroded or corroded by most agents. Still another object is the provision of an improved refractory body which can be simply and economically manufactured in quantity. The invention further provides a refractory body which can be easily manufactured in relatively complex shapes, as well as in the form of rods, bars and tubes and which lends itself to a wide variety of uses where oxidation, erosion and corrosion resistance at high temperatures is desired.

Heretofore, many different alloys have been proposed for the manufacture of refractory articles, but almost all of them have required casting at extremely high temperatures, have been inordinately expensive, or have been incapable of substantially resisting erosion, corrosion and oxidation at high temperatures.

Although the molybdenum silicides have been known as chemical compounds or alloys for over fifty years, their industrial application up to the present has been limited to their use as addition agents for introducing molybdenum and silicon into ferrous and other alloys, and aside from that use they have remained interesting laboratory curiosities.

Molybdenum silicides do not readily lend them-

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selves to the production of shaped articles by ordinary methods of casting or machining and the cast material is not sound, is porous and many large voids occur in the castings so that it is impractical to produce strong refractory objects from the cast metal or alloy.

I have now found that molybdenum silicide possesses the unusual property of being stable in oxidizing atmospheres at temperatures as high as about 1700° C. and that it is also resistant to the usual erosive and corrosive agents at high temperatures and by the process of the present invention, refractory articles may be readily, easily and economically produced from such molybdenum silicide.

In carrying out the process of the present invention crushed and powdered molybdenum silicide is mixed with a small proportion of an organic binder and with enough water to form a stiff composition which is then formed or molded to the desired shape, after which the formed articles are air dried and then are heated to ignite the binder and to sinter the remaining molybdenum silicide into a dense, strong mass which is substantially resistant to most of the usual eroding and corroding agents at ordinary and elevated temperatures. Due to the extraordinarily simple manner in which the molybdenum silicide may be formed and treated many refractory articles may be prepared much more economically than otherwise, and in many instances, the process of the present invention provides the most practical manner of forming many such objects of complex shape.

While molybdenum monosilicide (MoSi) and molybdenum sesquisilicide (Mo_2Si_3) may be used in putting the present invention into practice, I prefer to use the molybdenum bisilicide (MoSi_2) due to its noble character and its great stability at temperatures up to its melting point. When heated to high temperatures (from about 1000° C. 1700° C.) any excess of molybdenum or silicon occurring in the metallic compound or alloy is volatilized leaving the pure molybdenum silicide as a noble, refractory mass.

Any desired organic binder may be used which has the requisite strength to hold the powdered mass together while it is drying and sintering. Among the suitable binders are starch, flour, glue, gelatin, ethyl cellulose, cellulose acetate, with the appropriate solvents or swelling agents to render the binder adhesive and also to render the mixture of molybdenum silicide and binder moldable.

The molybdenum silicide is preferably crushed and ground to provide a relatively fine powder which is usually sufficiently fine to pass through a 200 mesh sieve. To the required amount of powder is added from 1/2 to 4% of the binder, and preferably about 1% of corn flour together with enough water, about 10 to 12% to form a stiff mud-like mass which can be manipulated, molded and shaped in the manner of ceramic clay.

Where other binders are employed, the quantities will be varied to give mixtures having the desired working properties and where binders such as cellulose acetate are used, organic solvents will be used.

The mass may then be formed into the desired shapes as by extrusion, rolling, molding or the like. Tubular objects are conveniently formed by extrusion; rods or bars may be formed by extrusion or by hand shaping and rolling, while hollow vessels and complex solid objects may be formed by molding or by working a mass with clay-sculpturing tools.

The shaped moist masses are preferably allowed first to dry until the objects are rigid, after which the objects are ignited to burn off the organic binder and finally the objects are sintered by heating them to a high temperature approaching the melting point of the molybdenum silicide. Thus using molybdenum bisilicide, the objects after shaping to the desired shape and drying are heated to approximately 1600° C. to 1900° C. which completes the sintering of the object in about 10 or 20 minutes, although for some sizes of objects shorter or longer periods of heating may be required.

Where the object is of substantially uniform cross-section such as a tube, rod or bar, the heating may be accomplished by passing electric current through the object to heat it by its own resistance. Thus using bars which are 4" long and about 1/8" in diameter, sufficient voltage may be applied to raise the temperature of the bar to about 1600° to 1900° C., with about 48 amperes flowing through the bar. Under these conditions the voltage drop across the bar was from 100 to 150 ohms.

Objects which do not have a uniform cross section may be heated slowly in a muffle or other furnace until the desired temperature and degree of sintering has occurred. In no instance is it necessary to maintain the molybdenum silicide objects in an inert atmosphere. The process of the present invention, as well as the refractory articles produced in accordance with the present invention thereby present a distinct and enormous advantage over sintered tungsten, which requires an inert atmosphere for its manufacture and use.

Among the many shaped objects which are usefully produced in accordance with the present invention are resistance heating elements, tubing for high temperature service, chambers for chemical reactions, electrical contacts, electric welding tips, fuel nozzles and orifices subjected to high temperatures, refractory linings for combustion chambers, structural members subjected to oxidizing conditions at extremely high temperatures of from 1500° C. to 1700° C. and similar uses where high temperatures are encountered along with severe erosion, corrosion and oxidizing conditions, but not including free halogen gases nor molten alkalis and alkaline earths.

Figure 1 illustrates schematically an electrical resistance element in accordance with the present invention and the resistance element 10 is formed of a uniform bar of molybdenum silicide, preferably the bisilicide, which is supported at its ends and connected in circuit by means of the enlarged and water-cooled terminals 12. The diameter and length of the bar element 10 are so proportioned that the element has the desired resistance to produce the desired temperature at the voltage to be supplied. The bar element 10, as distinguished from most high temperature re-

sistance heating elements, requires no protective coating or casing.

Figure 2 schematically illustrates another shaped refractory article in accordance with the present invention. As shown, there is provided a high-temperature oil-burner nozzle comprising a body portion 20 having a conical tip 22 with feed aperture 24 and a flat base portion 25 by which the nozzle is mounted on the end of the fuel supply pipe. In service, the nozzle is subjected to water vapor, carbon, oxygen, and other corrosive agents, is heated to high temperatures not only by the flame itself but from the radiation of the internal surfaces of the combustion chamber and is further subject to erosion by the oil and liquids passed through the nozzle. However, in spite of the severe conditions, and due to the refractory nature of the material, and its good heat conductivity, the nozzles have long life and give long periods of trouble-free service.

Such nozzles as are shown in Figure 2 are readily and economically made by the process of the present invention by forming the object from a stiff mixture of the powdered molybdenum silicide, the binder and binder solvent and by drying the shaped object which is initially formed sufficiently over size to allow for shrinkage in drying and sintering. Then the shaped object is heated to a temperature considerably higher than it will experience in service which completes the operation.

Due to the metallic nature of the sintered molybdenum silicides, the shaped refractory objects conduct heat easily, are thereby enabled to withstand rapid and great temperature changes and have good mechanical strength under operating conditions.

The invention in its broader aspects is not limited to the specific process, steps and mechanisms shown and described but departures may be made therefrom within the scope of the accompanying claim without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed is:

The process of forming a molded refractory article from molybdenum bisilicide, comprising the steps of grinding said bisilicide to about 200 mesh, mixing said ground material with water and an organic binder into a mud-like mass, molding said mass into the desired shape for the finished refractory article, air drying the molded article, and passing a heavy electric current through the article to heat it to about 1600°-1900° C. to ignite and drive off the binder and to sinter the molybdenum bisilicide.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,068,411	Heuer	Jan. 19, 1937
2,122,960	Schwartzwalder	July 5, 1938

FOREIGN PATENTS

Number	Country	Date
435,754	Great Britain	Sept. 23, 1935
294,267	Germany	Sept. 12, 1913

OTHER REFERENCES

Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," vol. 6, page 192, published 1925.