

Jan. 12, 1954

E. A. BEIDLER ET AL
HIGHLY REFRACTORY MOLYBDENUM ALLOYS
Filed March 18, 1950

2,665,474

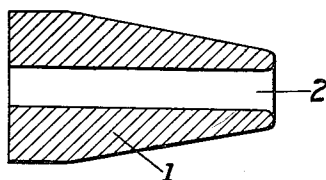


Fig. 1

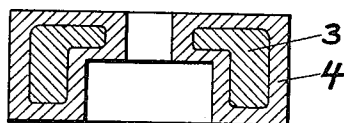


Fig. 2

EDWARD A. BEIDLER
IVOR E. CAMPBELL
INVENTORS.

BY *George F. Mueller*

UNITED STATES PATENT OFFICE

2,665,474

HIGHLY REFRACTORY MOLYBDENUM ALLOYS

Edward A. Beidler, Columbus, and Ivor E. Campbell, Gahanna, Ohio, assignors, by mesne assignments, to Fansteel Metallurgical Corporation, North Chicago, Ill., a corporation of New York

Application March 18, 1950, Serial No. 150,541

8 Claims. (Cl. 29—195)

1

This invention relates to solid, dense molybdenum alloy bodies having high strengths and a high resistance to oxidation, to thermal shock, to erosion of hot gases and to deformation at elevated temperatures.

The refractory metal molybdenum, has highly desirable properties and characteristics for many purposes and retains its normal mechanical properties at elevated temperatures. Molybdenum, for example, is very desirable for use in electric furnace heating elements, however, it is subject to oxidation at elevated temperatures and oxygen is excluded by maintaining a flow of hydrogen over the heated resistance element.

In the copending application of Campbell et al., Serial No. 150,398, filed March 18, 1950, entitled Highly Refractory Bodies, there is described and claimed a molybdenum body protected against oxidation at elevated temperatures by the provision of an integral coating or skin composed of molybdenum-silicon alloys. For some purposes, difficulties are encountered in producing a relatively thick and uniform alloy coating on the molybdenum to provide this integral protective skin. These difficulties are encountered particularly in the production of bodies of irregular configuration and complex sections.

The principal purpose of the present invention is to provide solid bodies formed of certain molybdenum alloys which bodies possess the aforementioned characteristics and properties at elevated temperatures.

Another purpose of this invention is to provide solid bodies of irregular configuration formed of certain molybdenum alloys.

Other objects and advantages of this invention will become apparent from the following description and claims.

In the drawings:

Fig. 1 is a cross-sectional view of a nozzle formed of the alloys of this invention.

Fig. 2 is a cross-sectional view of a large body formed of the alloys of this invention and including a reinforcing core.

The present invention contemplates the production of solid bodies formed of molybdenum-silicon alloys or intermetallic compounds, the silicon content of the alloys varying in the molecular ratio of silicon to molybdenum of from about 1:1 to about 3:1. This ratio corresponds to alloys

2

or intermetallic compounds of molybdenum and silicon containing from about 22% to about 47% silicon. The alloy or compound corresponding to a molecular ratio of silicon to molybdenum of about 2:1 or containing about 37% silicon appears to provide the most satisfactory bodies.

These alloys of intermetallic compounds may be formed by any desired method. One convenient method includes mixing molybdenum powder and silicon powder in the desired proportions in accordance with powder metallurgy practice. The mixture is then pressed into briquets and the briquets heated slowly to a temperature of about 1050° C. to about 1100° C. A rapid exothermic reaction occurs and continues to a temperature of about 1450° C. The rate of reaction and completeness of the reaction may be regulated by a control of the particle size of the molybdenum and silicon powders. The mass, after it is cooled, is quite porous and brittle and may be employed directly or may be converted into a granular or powder form.

The alloy or intermetallic compound so produced is melted as by heating in an arc-melting furnace or may be placed in a suitable crucible and heated by induction. The molybdenum-silicon alloys are quite reactive with many of the usual refractory materials employed for lining crucibles and furnaces at the temperatures required to render the alloys sufficiently fluid to permit pouring and casting. Thus, magnesia and beryllia are not satisfactory. Graphite apparently reacts with the molybdenum-silicon alloys to a sufficient extent so that the alloys when melted in contact with graphite become somewhat viscous. The alloys react sufficiently with graphite so that although they are heated in contact with graphite to temperatures as high as about 2200° C., the molten alloys do not possess sufficient fluidity to permit satisfactory casting. We have found that zirconia stabilized with calcium oxide is satisfactory as furnace and crucible linings and for the manufacture of crucibles.

The alloys may be cast in molds formed of graphite or zirconia. Since the alloys are generally cast at temperatures above 1800° C., the molds are preheated to a temperature of between 500° C. and 1000° C. before the molten alloy is poured into the mold to avoid chilling the hot mass too rapidly. In some instances, particularly

in forming bodies having relatively thin sections, graphite molds are less desirable because the higher heat conductivity of graphite results in an undesired rapid cooling.

We have found that when the alloys are melted there is an ebullition of gas, and this ebullition appears to continue until the alloy begins to solidify. Castings thus produced are porous and the degrees of porosity appears to vary inversely with the maximum temperature of the melt prior to pouring and with the period of time the material has been maintained in a molten condition. We have discovered that by heating the molten mass to a higher temperature for a brief period or by maintaining the mass molten for a prolonged period, the ebullition may be brought farther towards completion so as to provide substantially non-porous cast bodies. During the ebullition, the alloys appear to lose silicon and it may be necessary in some instances to add silicon so as to insure the desired silicon content in the finished cast bodies.

The cast bodies of the molybdenum-silicon alloys are somewhat brittle, particularly those cast in graphite molds due to the rapid cooling which results because of the high heat conductivity of graphite. The brittleness may be reduced by vacuum annealing, for example by heating the cast bodies in a vacuum to a temperature of about 1100° C. for 20 to 24 hours. During this vacuum annealing it is observed that gases are released from the bodies.

The cast bodies have a density of about 6.2 grams per cubic centimeter and a compressive strength of about 100,000 pounds per square inch at room temperature. The bodies retain a high strength at elevated temperatures. The bodies are extremely resistant to thermal shock, for example, the body may be rapidly heated to red heat by the use of a oxyacetylene torch and immediately quenched in water without exhibiting cracks. The body may be subjected to several such cycles without exhibiting cracks and because of the extremely high resistance to oxidation will exhibit no signs of surface oxidation. The bodies possess high thermal conductivity and high electrical conductivity. The physical and mechanical properties are retained at elevated temperatures and the bodies are extremely resistant to deformation at high temperatures.

Electrical heating elements must possess a high resistance to thermal shock, a high resistance to oxidation and must have a fairly high electrical conductivity. Cast bodies of molybdenum-silicon alloys are particularly advantageous as such heating elements because of their exceedingly high resistance to oxidation. The element may be formed from a cast rod of any desired diameter and length or may consist of a cast grid. Because of the high compressive strength, good electrical contact with the element may be obtained by means of suitable clamps.

As is well known, various types of nozzles, jets, and vanes intended for uses where they will be subjected to high velocity gases, such as erosive gases of combustion, must possess high resistance to oxidation and the erosive action of gases of combustion and must also be highly resistant to thermal shock. Such elements may be advantageously formed by casting the desired body from the molybdenum-silicon alloys as described hereinafter. As illustrated in Fig. 1, a nozzle 1 having a longitudinally extending aperture 2 may be formed by casting the alloy in a graphite

mold having a suitable core for forming the aperture.

For some bodies, particularly larger sized bodies, it may be desirable to increase the strength of the cast body. This may be readily attained by reinforcing the cast body with molybdenum or tungsten shapes. In the production of such bodies, the molybdenum or tungsten core or shape is supported in the mold in a conventional manner and the molten molybdenum-silicon alloy cast about the core. In order to prevent contamination of the alloy, rods of molybdenum-silicon alloy may be employed to position the core within the mold cavity. As shown in Fig. 2, the finished body consists of the core 3 about which the alloy 4 has been cast. It is apparent that the core may be an annular ring or may consist of spaced plates, the details being dependent upon the particular shape of the finished body.

It is to be understood that the foregoing description is intended to be illustrative of our invention and the specific examples included are set forth for purposes of illustration rather than as limitations of the invention.

We claim:

1. As an article of manufacture, a dense body of high strength and high resistance to oxidation, to erosion of gases, to thermal shock and to deformation at temperatures above about 1200° C., consisting of a substantially non-porous cast body of a molybdenum-silicon alloy, the alloy containing from about 22.5% to about 47% silicon.
2. As an article of manufacture, a dense body of high strength and high resistance to oxidation, to erosion of gases, to thermal shock and to deformation at temperatures above about 1200° C., consisting of a substantially non-porous cast body of a molybdenum-silicon alloy, the alloy containing about 37% silicon.
3. An electrical heating element consisting of a substantially non-porous cast body of a molybdenum-silicon alloy, the alloy containing from about 22.5% to about 47% silicon.
4. An electrical heating element consisting of a substantially non-porous cast body of a molybdenum-silicon alloy, the alloy containing about 37% silicon.
5. A nozzle for erosive gases of combustion consisting of a substantially non-porous cast tubular body of a molybdenum-silicon alloy, the alloy containing from about 22.5% to about 47% silicon.
6. A nozzle for erosive gases of combustion consisting of a substantially non-porous cast tubular body of a molybdenum-silicon alloy, the alloy containing about 37% silicon.
7. As an article of manufacture, a dense body of high strength and high resistance to oxidation, to erosion of gases, to thermal shock and to deformation at temperatures above about 1200° C., said dense body comprising a core selected from the class consisting of tungsten and molybdenum encased in a substantially non-porous casting of a molybdenum-silicon alloy, the alloy containing from about 22.5% to about 47% silicon.
8. As an article of manufacture, a dense body of high strength and high resistance to oxidation, to erosion of gases, to thermal shock and to deformation at temperatures above about 1200° C., said dense body comprising a substantially non-porous cast body of a molybdenum-silicon alloy, the alloy containing from about

2,665,474

5

22.5% to about 47% silicon, and a reinforcing core embedded in said cast body.

EDWARD A. BEIDLER.
IVOR E. CAMPBELL.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,718,563	Kelley -----	June 25, 1929
1,853,370	Marshall -----	Apr. 12, 1932
2,290,194	Linz -----	July 1, 1942
2,619,406	Briney -----	Nov. 25, 1952

5

6

FOREIGN PATENTS

Number	Country	Date
294,267	Germany -----	Sept. 25, 1916
435,754	Great Britain -----	Sept. 23, 1935

OTHER REFERENCES

Hansen: "Aufbau der Zweistofflegierungen,"
1936; page 912.
Wheeler: Metals Technology, August 1944
10 (pages 9 to 11 relied upon).