United States Patent Office 3,015,579
Patented Jan. 2, 1962

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3,015,579

METAL COATING PROCESS

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No Drawing. Filed June 15, 1959, Ser. No. 820,122
8 Claims. (Cl. 117—107)

This invention has to do generally with improved surface treatments of the refractory metals columbium and tantalum to prevent their destructive oxidation when exposed to air at high temperatures, and to reduce their tendency toward embrittlement through the absorption of gases.

It is well known in the art that the refractory metals, including also tungsten and molybdenum, can be rendered resistant to high temperature oxidation, by so-called siliconizing of the metal surfaces by either vapor phase ("vapor plating") or solid pack techniques, according to which a silicon halide is caused to react with the metal surface to deposit silicon and form a coating complex that may be composed of silicon, silicides or silicon alloys of the base metal.

We have found that for our purposes the pack method is advantageous over the vapor plating methods in that lower temperatures are employed, equipment is much simpler and more economical, continuous attendance of an operator is not required, and the size of the part that may be treated is not limited to the extent required in the vapor plating type of treatment. We have also found that in the pack siliconizing process, much greater dependency is placed upon reaction between the base metal and the active gases (silicon halide), and that the chemical properties of the base metal with respect to these gaseous components significantly affect the result. In vapor plating, the silicon halide gas is believed to be reduced by hydrogen and deposited, as in the nature of electroplating, upon the base metal being treated, whereas in the pack-type process, a reduction reaction or interchange reaction occurs. As a consequence of this difference, we have found it difficult to achieve the highest success desired in the surface treating and coating of columbium and tantalum with simple pack siliconizing treatments, whereas similar techniques have proven quite satisfactory as applied to molybdenum and tungsten. Our general object in the present invention is to modify the surface of columbium or tantalum parts, so that they will be receptive to the pack siliconizing processes at practically desirable temperatures. In referring to the metals columbium and tantalum, we intend to also include their alloys, by which term is meant alloy compositions containing preponderantly the base metal together with any of other various metals depending upon the nature and properties of the alloy desired. For example such alloys may be composed of either columbium or tantalum together with lesser percentages of the other metals or such non-refractory metals as iron, nickel, chromium, zirconium and others.

In accordance with the invention we first diffuse molybdenum or ferro-molybdenum (which may contain about 55 to 65% molybdenum and about 35 to 45% iron), into the surface of the columbium or tantalum by means of a pack diffusion application preceding the siliconizing treatment. This preliminary diffusion treatment produces what may be regarded as a primer coating of alloy rich in molybdenum or molybdenum and iron, having peculiarly advantageous chemical properties for reaction with silicon halide gases in a subsequent pack siliconizing process to finally form a satisfactory protective coating. The approach taken may appear unorthodox in that we employ the most reactive of all the refractory metals (molybdenum) insofar as its tendency for susceptibility to high

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temperature oxidation is concerned, to provide a basis for forming an oxidation-resistant coating on another refractory metal somewhat less prone to oxidation. However, the more active an element is in its pure state, generally the more stable are its compounds. Thus by surface alloying the less active element, e.g. columbium, with the more active element molybdenum, we are able to form more stable intermetallic compounds (molybdenum silicides) that exhibit superior protective properties, and do so by the simple solid pack process.

We have also found that the presence of iron in the "primer coating" tends to prevent embrittlement of the base metal, apparently due to absorption of gases during treatment or subsequent heating. This is particularly important in the instance of columbium, tantalum and their alloys, as room temperature ductility is a major advantage in these metals.

In more specific reference to the methods and materials employed in carrying out the invention, the refractory base metal piece is first ferromolybdenumized by heating at a temperature in the range of about 1600° F. to 2800° F. for from 3 to 20 hours in a powder mixture composed of about 30 to 50 parts by weight of ferro-molybdenum, 70 to 50 parts by weight of inert diluent, and about 0.02 to 5 parts of an inorganic halide, all solids being powdery and under about 60 mesh particle size. The inert diluent may be any of various materials known to be usable in the solid pack type of treatment, such as tabular alumina, silica, bentonite, bauxite, kaolin, crushed fire clay, chromite and the like. For our purposes, tabular alumina may be regarded as preferred. The halogen-containing component may be any of the different inorganic halides such as the halides of iron, copper, or ammonia, the anionic halides of course being chlorine, bromine, fluorine and iodine. We prefer the use of the ammonium halides, and specifically ammonium bromide.

The pack method involves placement of the refractory metal piece or pieces to be treated, in surface contact with the powder mixture in an impermeable box or retort of an appropriate heat-resistant metal provided with a fusible rim seal that melts during the heating cycle to allow excess gases to vent, and which solidifies upon cooling to prevent air from entering the box. The physical characteristics of this type of pack have long been known in the art.

Following ferromolybdenumizing of the base metal as described, the metal thus initially surface treated is removed from the pack and siliconized by a similar pack technique according to which the work metal is placed within the same kind of fusible rim box in contact with a powder mixture of from about 20 to 50 parts of silicon, 70 to 45 parts of inert filler such as tabular alumina, and 0.02 to 5 parts of an inorganic halide. As heretofore indicated, siliconizing of the previously treated metal surface results in the formation of a final coating on the base metal rendering the latter satisfactorily resistant to oxidation at high temperatures.

As specific examples of refractory metals treated in accordance with the invention, we prepared three samples, the first being composed of 0.5 weight percent zirconium, and the balance columbium; a second containing 0.5 percent zirconium, 39.5 percent tantalum and the balance columbium, and a third sample analyzing 16 percent molybdenum, 5.5 percent iron, 3.5 percent tantalum and the balance columbium. Specimens of each of these alloys were ferromolybdenumized by heating at 1900° F. for six hours in a powder mixture pack composed of 35 percent ferro-molybdenum (58.8% molybdenum and 41.2% iron), 65 percent tabular alumina and 0.3 percent ammonium bifluoride. Subsequently, the ferromolybdenumized specimens were siliconized by heating at 1850° F. for eight hours in a powder pack mixture composed of

35 percent elemental silicon, about 65 percent tabular alumina and 0.3 percent ammonium bifluoride. The specimens were subjected to static oxidation in air at 2400° F. with no observable breakdown of the coating or oxidation of the base metal, for periods up to one and one-half hours.

We claim:

1. The process of treating a refractory metal of the group consisting of columbium, tantalum and alloys thereof to render the metal surface resistant to oxidation at high temperatures, that includes, heating the metal to a temperature between about 1600° F. and 2800° F. in a non-oxidizing atmosphere and in surface contact with a powder mixture of about 30 to 50 weight parts of a substance of the class consisting of molybdenum and ferro molybdenum, about 70 to 50 parts of inert filler and 0.02 to 5 parts of an inorganic halide and thereby alloying molybdenum into the metal surface; and subsequently heating the metal to a temperature between about 1600° F. and 2800° F. in a non-oxidizing atmosphere with said surface in contact with a powder mixture of about 20 to 50 parts of silicon, 70 to 45 parts of inert filler and 0.02 to 5 parts of an inorganic halide to thereby form a molybdenum silicide protective surface coating.

2. The process of claim 1, in which said metal is columbium.

3. The process of claim 1, in which said metal is tantalum.

4. The process of claim 1, in which said ferromolybdenum contains about 55% to 65% molybdenum and about 35% to 45% iron.

5. The process of claim 1, in which said inert filler is alumina.

6. The process of claim 1, in which said halide is ammonium bromide.

7. The process of claim 1, in which said metal is columbium, said inert filler is alumina and said halide is ammonium bromide.

8. The product made according to the process of claim 1.

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