

1

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PROTECTIVE COATING OF REFRACTORY METALS

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This invention has to do with the protective coating of the refractory metals molybdenum, tantalum, tungsten and columbium, and alloys of those metals, for the purpose of rendering the base metal so treated, exceptionally resistant to oxidation and physical deterioration when maintained at high temperatures over long periods of time. More particularly, the invention is directed to a new method for achieving such protection by surface diffusion of other metals into the base metal, and the improved protectively coated products resulting from such diffusion.

For many modern purposes these refractory metals may be required to withstand high temperature heating in oxidizing atmospheres, under conditions tending to cause rapid or excessive oxidation of the metal unless it is surface protected. Considering, for example, parts made of molybdenum or a molybdenum alloy (typically molybdenum alloyed with around 0.5 percent titanium or zirconium), such parts may be required to operate in air or other oxidizing atmosphere in temperatures in the range of 1800° F. to 3600° F. and over periods of exposure to such temperatures that tend to produce failures, though they may be small and of a "pin hole" order, in protective coatings heretofore devised. While this type of failure might be tolerable in other metals not highly or violently susceptible to oxidation under such conditions, the oxides of molybdenum are gaseous in this high temperature range and even a very small fracture or interruption of an otherwise continuous protective coating, can become catastrophic in a short time.

Accordingly, our general object is to provide these refractory metals with a surface diffused protective coating having such assured continuity, resistance to interruptions however small, and resistance to high temperatures over extended exposure in oxidizing atmospheres, as to insure the base metal against physical or chemical impairment.

Generally considered, this object is accomplished by diffusing both silicon and boron into the base metal surface to depths corresponding to those achieved according to past techniques for diffusion of one metal into the surface of another, thereby to produce a protective coating in which the silicon, boron and base metal are interalloyed or combined, and the silicon and boron at the surface are alloyed in a state of continuously uniform distribution resulting in corresponding uniformity of the protection given the base metal.

While the invention contemplates generally the diffusion of the silicon and boron either simultaneously or sequentially into the base metal surface, we preferably employ a procedure calculated to assure uniformity in the final diffused state of these metals, by obviating any tendency for one to diffuse differentially to any consequential degree, by first combining the silicon and boron before their diffusion application to the base metal. Thus, as will appear, our preferred procedure is to heat together the silicon and boron in a non-oxidizing atmosphere at temperatures that may correspond to those employed for the subsequent diffusion, thereby to alloy the silicon and boron or complex them into the nature of a silicon boride, so that the two metals will have become

2

precombined in this sense and thereby caused to diffuse with greater assurance of uniformity, when subsequently heated against the base metal surface.

Our preferred practice for diffusion purposes is to heat the base metal in what physically is a well known form of pack comprising a metal box containing the parts to be treated in surface contact with a powdered mixture containing the silicon and boron to be diffused. Such mixtures include an inert diluent whose primary function is that of a partitioning medium between the active particles (silicon-boron), and a halogen source which according to known diffusion practices serves as a chemical mechanism in the metal diffusion. When the pack is heated in a furnace to the proper temperature, the silicon and boron diffuse into the base metal surface in a non-oxidizing atmosphere created preferably by gasified components of the halogen source, which are released by reason of the box design and seal which excludes oxygen but permits release of excess generated gases.

Good results have been obtained by first mixing together and alloying the powdered silicon and boron in a non-oxidizing atmosphere and at a temperature and time that may correspond to the range employed for the subsequent diffusion. For this purpose we may keep together the uniformly mixed silicon and boron powder in the same kind of retort as that used in diffusing the resulting alloy into the base metal.

As indicated, the base metal may be of the group consisting of molybdenum, tantalum, tungsten and columbium, or any of these metals alloyed with small percentages of other metals such as titanium and zirconium, or with other of these same refractory metals. The base metal to be surface protected may have any of various physical forms such as nozzles, blades, vanes, shells or other configurations which in use undergo exposure to high temperatures, say in the range of about 1800° F. to 3600° F.

The silicon source employed preferably is powdered elemental silicon in the range of 60 to 325 mesh, or other powdered silicon sources such as ferro-silicon, from which the silicon is releasable for alloying with the boron.

The boron source preferably is amorphous boron or corresponding (60 to 325 mesh) fineness, although we may employ ferro boron, or boron in other form from which the elemental boron is available for alloying, as such, with the silicon.

The halogen source to be used in the diffusion pack may be any one or more of the halogens or halogen-releasing compounds commonly used in diffusion techniques of this character. Such compounds are known to release halogen under the treatment conditions for combination with the metal being diffused and with the base metal itself. The conventionally employed halogens and halides include fluorine, chlorine, bromine, iodine, and the metal and ammonium salts of each. Without intending limitation, we may state a preference for the use of ammonium bifluoride in the present process, particularly as applied to the surface protection of a base metal which is essentially molybdenum.

The diluent component of the powdered pack mixture may be any of various refractory materials in finely divided or powdered form, and having a mesh size from about 50 to 350 mesh. Clay, kaolin, zirconia, beryllia, and tabular alumina are illustrative.

Speaking in terms of the diffusion pack composition, the latter may contain about 5 to 70% silicon (calculated as elemental silicon component of the pre-formed boron silicon alloy), about 1/8% to 10% boron, similarly calculated as elemental boron, between about 0.1% to 1.0% halogen source, with the remainder inert diluent, in the

3

range of about 25 to 75%, all percentages being by weight.

According to our preferred procedure, the finely powdered boron, silicon, halogen source and diluent are uniformly admixed and heated in the absence of oxygen within the temperature range of about 1600 to 2200° F. over a period of time, say in the range of 8 to 12 hours, required to uniformly alloy or complex these metals (i.e. the silicon and boron). The resulting finely powdered silicon-boron alloy is then mixed uniformly with a new charge of halogen source of the same proportion to form the diffusion pack composition. The latter is packed in direct contact with the base metal in a retort box as described, and the latter, with its contents, is heated to a temperature in the 1600° F. to 2200° F. range over a period of about 8 to 12 hours. As a result of the heating, the boron and silicon are caused to diffuse into the base metal surface and to alloy or combine with the base metal, physically to a state such that the alloyed base metal, silicon and boron form a fully continuous protective coating, which I have found to be extraordinarily resistant to high temperature oxidation or physical rupture.

The following are examples illustrative of the invention:

Example I

Three pieces of molybdenum alloy of the approximate composition 0.5% Ti, 0.07% Zr, balance molybdenum, were treated by diffusion into their surfaces of three separately prepared interdiffused boron-silicon compositions made by heating in a retort box at about 1800° F. for 5 hours, a mixture of 34% silicon powder, 65% tabular alumina, ¼% ammonium bifluoride, and

Composition A-----1% amorphous boron powder
Composition B-----3% amorphous boron powder
Composition C-----5% amorphous boron powder

(These percentages being by weight of the total mixtures.)

The three molybdenum alloy samples were packed in separate treatment boxes respectively with the combined silicon-boron resulting from the compositions A, B and C, above (separated from the residual alumina and bifluoride), together with fresh alumina and bifluoride in similar proportions, i.e. in each instance with about 65% alumina and ¼% ammonium bifluoride, the remainder silicon-boron.

Each molybdenum alloy specimen, so packed, was heated to 1800° F. for 12 hours. The boxes were allowed to cool and were opened and the specimens were unpacked and brushed clean. The specimens were tested by heating in slowly moving air at 2000° F. for 3500 hours, removing the specimens every 24 hours and allowing cooling to room temperature for visual examination. At the end of 3500 hours no sign of failure was visible on any specimen.

Example II

A specimen of molybdenum alloy 0.5% Ti, balance molybdenum, was treated using composition A, above, and tested by heating with oxy-acetylene torch to 3000° F. in 25 seconds and holding temperature for 60 seconds. After 21 cycles of heating, there was no observed failure.

Example III

A specimen of molybdenum alloy 0.5% Ti, balance molybdenum, was treated. It was tested by heating in slowly moving air at 2700° F. The coating withstood 175 hours of testing without failure.

Another specimen of this same composition was subjected to 10 successive heatings to 500° F. and quench-

4

ings to minus 300° F. in liquid oxygen within ½ second, and then to 10 additional successive heatings to 2500° F. and quenchings to minus 300° F. in 1 second. No failures in the specimen could be observed.

We claim:

1. The process of protectively coating a refractory base metal of the group consisting of molybdenum, tantalum, tungsten and columbium, and alloys of those respective metals, that includes heating the base metal at a temperature between about 1600° F. and 2200° F. in a non-oxidizing atmosphere and in contact with a powdered mixture of an inert solid diluent, a halogen source and both boron and silicon distributed in said mixture in condition from which the boron and silicon are diffusible into the base metal, and thereby diffusing silicon and boron into the surface of the base metal to form a continuous protective coating integrated therewith.

2. The process of claim 1, in which said powdered mixture contains between about 5% to 70% silicon calculated as elemental silicon, between about ¼% to 10% boron calculated as elemental boron, between about 0.1% to 1.0% halogen source, and between about 25% to 75% of said inert diluent.

3. The process of claim 2, in which said base metal is essentially molybdenum and said halogen source is ammonium bifluoride.

4. The process of claim 1, in which said base metal is essentially molybdenum.

5. The process of claim 1, in which said silicon and boron are integrated in said powdered mixture.

6. The process of claim 1, in which said silicon and boron are integrated in said powdered mixture, and said base metal is essentially molybdenum.

7. The process of protectively coating a refractory base metal of the group consisting of molybdenum, tantalum, tungsten and columbium, and alloys of those respective metals, that includes heating together powdered silicon and boron in a non-oxidizing atmosphere and distributed in a powdered mixture of an inert diluent and a halogen source at a temperature between about 1600° F. and 2200° F., then heating the base metal in a non-oxidizing atmosphere at a temperature between about 1600° F. and 2200° F. with a powdered mixture containing the silicon and boron resulting from said heating together with inert diluent and a halogen source, and thereby diffusing silicon and boron into the base metal to form a continuous protective coating integrated therewith.

8. The process of claim 7, in which said base metal is essentially molybdenum.

9. The process of claim 7, in which said halogen source is ammonium bifluoride.

10. The process of claim 7, in which the last mentioned powdered mixture contains between about 5% to 70% silicon calculated as elemental silicon, between about ¼% to 10% boron calculated as elemental boron, between about 0.1% to 1.0% halogen source, and between about 25% to 75% of said inert diluent.

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