OXIDATION-RESISTANT COATINGS
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4 Claims

ABSTRACT OF THE DISCLOSURE
An oxidation-resistant coating for articles of refractory metals and alloys comprising an underlayer rich in iridium, and a top layer of glaze.

BACKGROUND OF THE INVENTION
This invention relates to oxidation-resistant coatings for articles of refractory alloys, particularly of niobium and of tantalum. In this specification the term "refractory alloys" includes essentially unalloyed refractory metals where the context permits.

Oxidation-resistant coatings have been suggested in which an underlayer of a modified metallic disilicide is applied to the article, the metal of the disilicide being the same as that of the article, e.g. modified niobium disilicide for niobium alloy articles. The underlayer is protected by a glaze coating from the atmosphere. In this way the glaze coating acts as the primary barrier to oxygen diffusion, but should there be any flaw in that coating, the modified metallic disilicide will serve as a second barrier.

This suggestion has been found to work satisfactorily in practice, but it suffers from two disadvantages of which the first is the gradual embrittlement of the glaze layer by reaction therewith of the modifying elements of the modified metallic disilicide layer, and of which the second is the fact that, at temperatures of the order of 1200° C., the silicon of the disilicide layer diffuses into the article itself, whereby there is left a silicon depleted underlayer which has a significantly lower oxidation resistance, and has a reduced resistance to diffusion of oxygen. Furthermore, all disilicide coatings are brittle.

Consequently, it is an object of the invention to provide an improved oxidation-resistant coating which suffers to a far smaller degree from the above two disadvantages.

SUMMARY OF THE INVENTION
In accordance with the invention, an oxidation-resistant coating for articles of refractory alloys comprises an underlayer of the alloy 100–0 wt. percent iridium and 0–100 wt. percent rhodium with incidental impurities, and at least one upper layer of glaze.

Preferably, the alloy of the underlayer contains at least 50 wt. percent iridium.

Preferably also the coating further comprises an intermediate layer located between the underlayer and said upper layer and comprises a material selected from the group consisting of alumina, hafnia, zircon, and zirconia.

The invention also consists in refractory alloy articles provided with oxidation-resistant coatings as defined in any one of the three next preceding paragraphs.

The invention further consists in a method of applying an oxidation-resistant coating to a refractory alloy article comprising applying as an underlayer of the alloy 100–0 wt. percent iridium and 0–100 wt. percent rhodium with incidental impurities to the article, and subsequently applying at least one upper layer of glaze.

The invention, as mentioned above, specifically relates to alloys of niobium and of tantalum, within which phrases are included substantially pure niobium articles and substantially pure tantalum articles. Thus, in accordance with the invention also, a niobium alloy article is provided with an oxidation-resistant coating comprising an underlayer 0.0001 to 0.0005 inch thick of the alloy 50 wt. percent approximately iridium and 50 wt. percent approximately rhodium with incidental impurities, and at least one upper layer of siliceous glaze, and in accordance with the invention further a tantalum alloy article is provided with an oxidation-resistant coating comprising an underlayer 0.0001 to 0.0005 inch thick of iridium with incidental impurities and at least one upper layer of siliceous glaze.

DESCRIPTION OF THE PREFERRED EMBODIMENTS
In a first typical example of the invention, a sheet specimen of the niobium alloy containing 11 wt. percent tungsten, 3 wt. percent molybdenum, 2 wt. percent hafnium was prepared for coating by radiusing the edges and corners by hand filing and by treatment in a rotor-finishing barrel. The specimen was then cleaned and its surfaces roughened by jet blasting with a mixture of air, water and coarse alumina powder.

The sheet specimen was then provided with a layer of iridium by electro-plating in a bath prepared by dissolving hydrated iridium dioxide (IrO$_2$•2H$_2$O) in a 0.1 mole/litre excess of hydrobromic acid and adding 5 grams/litre of ammonium bromide. The bath contained 5 grams/litre of tetravalent iridium and had a pH of 2–3.

At a temperature of 75° C. and a current density of 0.2–0.3 amperes/cm$^2$, 2–3 hours of plating time using an insoluble iridium anode produced a layer of iridium between .0001 and .0005 inch in thickness.

After electro-plating, the specimen was provided with a sprayed-on intermediate layer of material selected from the group consisting of alumina, hafnia, zircon and zirconia. It will be appreciated by the man skilled in the art that the selection of the material to be used for this intermediate layer depends principally upon the base material: for niobium, alumina has approximately the correct thermal expansion coefficient whilst zirconia is the least satisfactory. The intermediate layer is preferably between 0.01 and 0.02 inch in thickness.

The specimen was then provided with an upper layer of siliceous glaze by spraying a suspension of a suitable siliceous glaze powder. In this example the glaze powder was suspended in toluene containing 5 wt. percent "Bedacryl" obtainable from Dyestuffs Division of Imperial Chemical Industries Limited, but a mixture of water and acetone can be used. In this example also, the glaze powder was the standard matt glaze produced by Steatite and Porcelain Products Limited with the composition by weight as follows:

<table>
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<tr>
<th>Component</th>
<th>Percent</th>
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<tbody>
<tr>
<td>SiO$_2$</td>
<td>62.1</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>23.4</td>
</tr>
<tr>
<td>MgO</td>
<td>1.5</td>
</tr>
<tr>
<td>MnO</td>
<td>1.1</td>
</tr>
<tr>
<td>CaO</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>3.7</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>1.1</td>
</tr>
<tr>
<td>Volatiles</td>
<td>4.8</td>
</tr>
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</table>

The siliceous glaze upper layer so formed was fired in vacuum at 1450–1600° C. for 15 minutes. A second upper layer was formed in the same way as the upper layer just described.
The siliceous glaze acts as a primary oxidation-resistant barrier, and is securely bonded in position by the intermediate layer. Even without the intermediate layer, the glaze bonds well to the iridium, although the intermediate layer does give some strengthening of the coating. The iridium is extremely resistant to penetration by oxygen, and resists oxidation to a very high degree. For example, it has been found that iridium resists oxidation in argon atmospheres containing 1% oxygen at up to 2000° C. In addition, the iridium does not react with the glaze where substantially no diffusion of iridium into the substrate. Furthermore the iridium is ductile so that it resists cracking, and its coefficient of thermal expansion is close to that of niobium.

In a modification of the first typical example, an underlayer of about 50 wt. % iridium and 50 wt. % rhodium with incidental impurities is used. The coefficient of thermal expansion of such an underlayer is almost exactly the same as that of niobium. This underlayer is produced by electro-plating from a hydrobromic acid bath, the bath containing 5 grams/litre of rhodium as well as of iridium, the rhodium being dissolved into the hydrobromic acid in the form of rhodium hydroxide. The same plating conditions are used to again produce an underlayer 0.0001 to 0.0005 inch thick, except that the underlayer will contain approximately equal parts of iridium and rhodium; some adjustment of pH, current density and temperature may be necessary to obtain the required equal parts of iridium and rhodium.

Specimens prepared in accordance with the typical example and with the modification thereof, with and without any intermediate layer were tested by exposure at 1200° C. to air for 100 hours. It was found that the hardness of the niobium alloy only increased to a negligible degree as compared to a similar experiment in which the iridium and iridium-rhodium was replaced by modified niobium disilicide. In the latter case, it was found that the alloy hardness increased to over 600 Vickers hardness as a result of oxygen penetration, and considerable reaction occurred between the glaze and the modifying elements of the niobium disilicide.

The oxidation-resistant coating described above is applicable to other refractory metals and alloy articles, particularly tantalum. Thus, in a second typical example of the invention, a sheet specimen of the alloy tantalum 10 wt. percent tungsten with incidental impurities was treated in exactly the same way as described in the typical example, except that, for tantalum, zirconia is the most satisfactory material for the intermediate layer as it has approximately the same coefficient of thermal expansion as tantalum. It should be noted, however, that an underlayer of iridium has a coefficient of thermal expansion which is nearer to that of tantalum than any alloy of iridium with rhodium.

Testing in air for 100 hours at 1200° C. showed only a negligible increase in the hardness of the tantalum alloy through oxygen penetration compared to a very large increase in a comparative specimen using tantalum disilicide instead of tantalum. Again there was no reaction between the iridium and the glaze.

We claim:

1. A refractory alloy article provided with an oxidation-resistant coating comprising an underlayer of the alloy 100–0 wt. percent iridium and 0–100 wt. percent rhodium with incidental impurities, and at least one upper layer of siliceous glaze.

2. An article according to claim 1 wherein the alloy of the underlayer contains at least 50 wt. percent iridium.

3. A niobium alloy article provided with an oxidation-resistant coating comprising an underlayer 0.0001 to 0.0005 inch thick of the alloy 50 wt. percent approximately iridium and 50 wt. percent approximately rhodium with incidental impurities, and at least one upper layer of siliceous glaze.

4. A tantalum alloy article provided with an oxidation-resistant coating comprising an underlayer 0.0001 to 0.0005 inch thick of iridium with incidental impurities and at least one upper layer of siliceous glaze.

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