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PROTECTIVE COATINGS FOR METAL SUBSTRATES

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ABSTRACT OF THE DISCLOSURE

Refractory metals, especially columbium, can be protected from oxidizing atmospheres by forming a continuous layer of refractory metal disilicide on the exposed surfaces. Such coatings can be made by forming the subsilicide of the refractory metal and then converting at least a part of the subsilicide to the corresponding disilicide.

BACKGROUND OF THE INVENTION

Field of the invention

The use of refractory metals and refractory metal alloys for high temperature applications is extremely desirable because such metals maintain their structural stability even at very high temperatures. They lack resistance to oxidation, however, and their applicability is limited by the environment in which they are used. Such resistance has been provided by the use of protective coatings upon the metal so as to separate the oxygen-prone substrate from an oxidizing atmosphere. Since parts formed of such metals are generally used in locations where they are subjected to very high temperatures, the coatings that are placed upon the surface must be truely flaw-free.

Many coatings have been developed which are capable of protecting refractory metals for hundreds of hours at elevated temperatures. Some of these coatings are based upon the principle that the silicides or aluminides of refractory metals resist oxidation. (In another approach, coatings of the intermetallic compounds of the refractory metals and silicon, boron, aluminum and combinations thereof have been used to resist oxidation.) Moreover, it has been conventional to form silicide coatings upon the refractory metals by reacting the substrate with a source of silicon. Each of these processes provided protection of the substrate for a limited period of time.

Generally, it has been found that such coatings failed to protect the substrate because of cracks which were initially present and gradually enlarged during use. The oxidizing atmosphere permeated the cracks, lifted the coating and exposed fresh substrate metal to the oxidizing environment ever enlarging the rupture. Such crack propagation, and also spalling, frequently occurred when the substrate was struck since the silicides of the refractory metals are hard and strong but not very ductile, when compared to most metals and alloys. Thus, as a result of the lack of ductility, these silicon coatings were rather prone to failure upon impact. Irrespective of the way the substrate fails, whether it be by initially occurring cracks or subsequently caused due to some impact, the refractory coatings do not fail in a uniform manner. Sometimes, however, they gradually wear out or the coating is consumed by a uniform oxidation. The local failures occur as cracks formed during processing which propagate slowly during normal oxidation or rapidly upon impact.

It is the intention of the present invention to provide reliable coatings for refractory metals and alloys in which the inherent defects are removed, thereby preventing oxygen from contacting the substrate.

SUMMARY OF THE INVENTION

According to the present invention, we have discovered that the tiny cracks which occur in silicide coatings on refractory metals and refractory metal alloys are not necessarily due to the stresses resulting from the differences in coefficients of thermal expansion between the coating and the substrate. Rather, we have found that they are caused by extremely large stresses that are produced because of the differences of specific volume between the substrate and the coating. For example, we have found that cracking, blistering or tearing occurs when the ratio of specific volume of refractory metal disilicide to the specific volume of refractory metal substrate is greater than about 2.0 due to the compression of the coating into a volume smaller than its equilibrium volume. Conversely, good adherence is obtained from coatings which have a specific volume ratio (relative to the substrate) between about 1 and 2. Below about 1, the coating will frequently crack due to the inability of the coating to cover the surface from which it is forming.

In the specific case of coating columbium (and columbium base alloys) with silicon, we have found that cracking occurs when columbium disilicide is coated on the columbium substrate. The ratio of specific volume of columbium disilicide to the specific volume of columbium is greater than 2.5. The columbium disilicide layer forms when the silicon is deposited upon the columbium substrate, due to an inward migration in which the silicon reacts with the substrate. Through this reaction, a layer of columbium disilicide forms which can crack and tear and thus is not suitable for use as a barrier in an oxidizing atmosphere at elevated temperatures.

On the other hand, we have found that the subsilicide of columbium (Cb_5Si_3) forms by an outward diffusion of the columbium from the substrate. The ratio of specific volumes of columbium subsilicide to columbium is about 1.56 and thus a continuous coating will be formed which will not crack or tear away. The subsilicide layer can be formed by any of the conventional techniques such as pack cementation, cold-spray slurry, chemical vapor deposition or similar processes provided that, as is well known, the chemical activity of the silicon source which is used is higher than that of the subsilicide to be formed, but lower than or equal to that of the disilicide.

The columbium subsilicide layer, however, does not effectively withstand oxidation and we have discovered that further treatment is necessary. We have found that the subsilicide can be converted to a disilicide layer in order to protect against such environments without cracking. Since the ratio of specific volume of columbium disilicide to columbium subsilicide is about 1.42 it can thus be seen that a protective coating can be formed by a conversion. Such conversions are performed, as is well known, by reacting the subsilicide coating with a source of silicon in which the activity of the source is equal to or greater than that of the disilicide layer to be formed. Usually pure silicon is employed.

Since the ratio of the specific volume of the subsilicide layer to the specific volume of the base metal is less than 2 and since the ratio of specific volume of the disilicide phase to the subsilicide phase is also less than 2, cracking does not occur and the substrate will be protected from oxidation. When a disilicide coating is formed directly upon the substrate, as we have noted above, the protective disilicide layer is formed by inward diffusion of silicon into the refractory metal. This disilicide coating during its formation expands to a point where it cracks or spalls and the problems are particularly noticeable around the edges of the substrate where coatings from two sides abut against each other and tend to force each other from the substrate. On the other hand, the subsilicide

coatings form on the surface by outward diffusion of the columbium. As such, they adhere more tenaciously to the substrate and do not expand the volume of the coating at the edges.

Thus, in recapitulation, the present invention involves forming a crack-free refractory metal subsilicide coating upon a refractory metal substrate by reacting the substrate with a silicon containing compound in which the chemical potential of the silicon is higher than that of the subsilicide to be formed but lower than or equal to the corresponding disilicide. From there, the subsilicide-coated, refractory metal substrate is reacted with a silicon source in which the activity of the silicon is equal to or greater than that of the disilicide layer to be formed (generally silicon metal). The conversion of the subsilicide to the crack-free disilicide is utilized because the latter is more resistant to oxidation than the former, but the ratios of specific volumes of the subsilicide to the substrate and in turn the disilicide to the subsilicide are each between 1 and 2 and hence cracking will be eliminated whereas a direct coating of the disilicide would crack from the refractory metal substrate because the ratio of specific volumes is greater than 2. The specific techniques that are used to form the subsilicide and disilicide coatings are important only insofar as continuous coatings are formed. Any conventional techniques for forming these coatings can be used: pack cementation, slurry, vapor deposition or spraying processes.

In the preferred process for preparing silicon coatings on columbium, the refractory metal is embedded in a source of columbium disilicide and heated, according to conventional pack cementation techniques, to form the crack-free columbium subsilicide (Cb_5Si_3). Frequently, up to 25 w/o of titanium, molybdenum, chromium or vanadium can be added because these metals can significantly improve the oxidation characteristics. Such mixed coatings have specific volumes, or their respective subsilicide compounds, which are even less than the columbium subsilicide. Then the disilicide coating is formed from the subsilicide coating by reacting the subsilicide coated substrate with a source of silicon whose chemical activity is greater than that of the disilicide, preferably elemental silicon. Care must be taken not to convert all of the subsilicide to the disilicide or else cracking will occur because the silicon will react directly with the substrate. At least about 10% of the subsilicide must remain.

To prove the effectiveness of the coatings of the present invention, two samples were prepared. The first had only a columbium disilicide coating while the second had the subsilicide coating which was converted to the continuous disilicide. Both coatings were about 1 mil thick and both samples were placed in flowing oxygen at 2000° F. Failure was determined by the presence of Cb_2O_5 exuding from cracks which occurred. The first failed in less than 100 hours, whereas when the test was discontinued at 250 hours the second specimen had not yet failed.

In a dynamic test, similar parts were exposed to exhaust gases from a simulation of gas turbine combustion. The first type of coating wore off at the rate of 10 hours/mil whereas the second was crack-free and wore off at the rate of 15 hours/mil.

DESCRIPTION OF PREFERRED EMBODIMENTS

The following examples are offered as a further explanation of the invention.

Example I

Twenty samples (4 each) of columbium and columbium base alloys were treated according to the present invention. These samples were:

Elemental columbium
Cb-1Zr (Cb-1% Zr
FS 85* (Cb-28% Ta-10% W-1% Zr)
B 66* (Cb-5% V-5% Mo-1% Zr)
C 129 Y* (Cb-10% W-10% Hf-0.1% Y)

*Commercially available columbium base alloys.

The samples in the shape of flat panels (1" x 1" x .030") were packed in a retort containing a blend of 20 volume percent $CbSi_2$, 80 volume percent Al_2O_3 and 0.5 gm. NH_4Cl. The retort was heated to 2300° F. for 150 hours. When the samples were recovered, they were uniformly coated with 0.8 to 1.0 mil thick layer of Cb_5Si_3.

The coated samples were then packed in the retort with elemental silicon and 1 w/o sodium fluoride as an acceleration. The retort was heated to 2000° F. for 2 hours to convert the Cb_5Si_3 to $CbSi_2$. Metallographic examination of the part indicated that it was crack-free and that 80% of the Cb_5Si_3 had been converted to $CbSi_2$.

Example Ia

A tungsten sheet, 1" x 1" x .090" was placed in the retort with the columbium base alloys. A W_5Si_3 coating was formed, as described above, which was subsequently converted into a crack-free WSi_2 coating, also as described above.

Example II

The same specimens as described in Example I (2 each) were placed in a retort filled with the same blend. The retort was heated to 2600° F. for 10 hours and Cb_5Si_3 of 2 mils thickness was formed. The conversion to $CbSi_2$ was the same as in Example I except that the samples were heated for 2½ hours. Crack-free columbium disilicide coatings were formed.

It is apparent that modifications and changes can be made within the spirit and scope of the present invention, but it is our intention only to be limited by the following claims.

As our invention we claim:

1. The process of protecting the surface of refractory metals selected from the group consisting of columbium, tungsten, and alloys thereof from oxidizing atmospheres and providing a substantially crack-free coating thereon, the steps which comprise:

forming a coating of a subsilicide of said refractory metal on said surface by exposing said surface to a source of silicon having a chemical activity higher than that of the subsilicide to be formed but not exceeding that of the disilicide, and then,

converting at least a portion of but not more than 90 percent of said subsilicide in terms of its thickness to the corresponding disilicide by reacting the subsilicide with a source of silicon having a chemical activity not less than that of the corresponding disilicide, said disilicide coating being substantially continuous and free of cracks,

whereby the surface can be protected from oxidizing atmospheres.

2. The process according to claim 1 wherein up to 80 w/o of said subsilicide is converted to the disilicide.

3. The process according to claim 1 wherein the silicon source for converting the subsilicide to the disilicide is elemental silicon.

4. The process according to claim 1 wherein said substrate is columbium and the layers which are formed on the subsilicide and disilicide of columbium.

5. The process according to claim 4 wherein a pack cementation process is used to coat said columbium surface with disilicide and subsilicide coatings.

6. The process according to claim 1 wherein a pack cementation process is used for coating said surface with silicon.

References Cited

UNITED STATES PATENTS

3,293,068 12/1966 Bradley et al. ..... 117—69

OTHER REFERENCES

Chemical Abstracts, vol. 64:9358e (1966).
Chemical Abstracts, vol. 56:3236c (1962).

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117—106 A; 148—6.3