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OXIDATION RESISTANT MOLYBDENUM BASE ALLOY

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This invention relates to molybdenum base alloys having a high resistance to oxidation at temperatures up to 2500° F. even after prolonged or intermittent exposure to oxidizing atmospheres at such temperatures and to a method whereby molybdenum is protected from destructive oxidation.

More particularly, it relates to alloys of molybdenum with at least one element from the group of elements which function as oxidation retarders or stabilizers and which consists of beryllium, titanium, aluminum, zirconium, chromium, silicon and vanadium in amounts up to about 6% by weight and at least one of a second group of elements which functions as a diffusion barrier and which may be present in amounts from an effective percentage up to about 1.0% and selected from the group consisting of calcium, cerium, erbium, lanthanum, neodymium, praseodymium, lead, or tin.

Molybdenum and molybdenum base alloys possess high temperature strength properties which make these metals desirable for many end uses. Unfortunately it has been found that these desirable properties are accompanied by poor oxidation resistance. When pure molybdenum or many molybdenum base alloys are exposed to oxidation at high temperatures, coatings form on the surface ranging from possibly MoO to and including MoO₃. At about 1200° F., MoO₃ volatilizes and continually exposes fresh metal to the oxidative conditions so that the destruction of the base metal as the result of oxidation tends to become catastrophic.

One previously proposed means for overcoming this poor oxidation resistance has been to clad the molybdenum or molybdenum base alloy article with a suitable oxidation resistant alloy. This approach has not been entirely successful because diffusion between the cladding material and the molybdenum base has often produced brittle interfaces which did not withstand repeated thermal cycling and which in many instances ultimately failed by actual physical separation of the clad from the base.

Still another disadvantage in the prior efforts to clad molybdenum and molybdenum base materials has been inherent in the brittleness of the cladding materials themselves. This has seriously limited the use of such coatings in applications where the article to be protected is subject to bending stresses.

One object of this invention is to provide a means for protecting molybdenum and molybdenum base alloys against oxidation at elevated temperatures and particularly against oxidation in environments in which the protective member is subject to repeated heating and cooling and to bending stresses.

Another object of the present invention is to provide a technique for selecting alloy compositions which will result in members possessing a combination of inherent properties which prevent the destructive oxidation of the molybdenum base material.

In order to develop a system applicable to the protection of molybdenum and molybdenum base alloys, it has been found that a double barrier must be provided to

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accomplish the required properties. Two distinct functions must be performed by the alloying elements added to the base whether applied as coating material or incorporated into the base as an alloying addition. The first of these functions is to retard or stabilize the oxidation and the second is to bar diffusion. The two additives may be described in terms of their chemical and physical properties relative to molybdenum and its compounds.

The first additive characterized by me as a stabilizer or retarder must be selected from elements having atomic volumes or radii less than the atomic volume or radius of molybdenum, so that ions or atoms of the additive will diffuse as fast as the base metal. Furthermore, the heats of formation of the oxides of the additives should be preferably greater than the heat of formation of the molybdenum oxide which forms when the base metal is exposed to oxidation.

The second additive, characterized by me as a diffusion barrier, must be selected from elements whose atomic volumes are greater than the molecular volume of the oxide which first appears on the surface of the molybdenum base article when it is exposed to oxidation. Furthermore, this additive should be selected from elements whose oxides have high heats of formation relative to the heat of formation of molybdenum oxide and whose oxides are refractory in nature and are capable of forming compounds with the first oxide which appears on the surface to be protected. The resulting compounds must themselves be refractory in nature for the proper protection to be achieved.

When an alloy has been prepared with suitable content of an element or elements from the first above described group and the second above described group, the following process takes place as soon as the resulting alloy is heated in an oxidizing atmosphere. First, an oxide will appear on the surface of the article and, in molybdenum-rich systems such as those presently contemplated in which the molybdenum content comprises substantially at least 90% by weight of the alloy, this oxide is apparently a suboxide of molybdenum. On continued heating the atoms of the stabilizer or retarder additive or additives diffuse rapidly through the superficial film of molybdenum suboxide to the outside and thereupon form an oxide as a result of contact with the oxygen or oxidizing environment. In addition to protecting the base metal from further oxidation by the formation of this oxide, the additive atoms which are present in the molybdenum oxide lattice maintain the structure and composition of the molybdenum suboxide and thus avoid the continued destructive oxidation characteristic of untreated base material. In this connection the higher heat of formation of these oxides relative to the heat of formation of the molybdenum oxide is additionally responsible for maintaining the stability of the molybdenum suboxide film.

Suitable stabilizers, as has been previously indicated, may consist of one or more of the following: beryllium, titanium, aluminum, zirconium, chromium, silicon and vanadium.

Each of the recited elements is capable of reducing higher oxides of molybdenum not only to the monoxide but also to the metal and each of the stabilizers listed may be added from effective amounts up to about 6% by weight of a total of the listed elements.

As a result of diffusion of both molybdenum and stabilizer atoms from the surface of the base metal into the oxide layer, a substantial increase of concentration of atoms of the second additive, above described by me as the diffusion barrier, is available just at the surface on the base metal under the oxide layer.

The second additive is selected from those elements having atomic volumes greater than the molecular volume of molybdenum suboxide, and as a result it blocks any

openings that may be available in the molybdenum suboxide structure. As a result, the molybdenum atoms of the base metal can no longer diffuse through the molybdenum oxide structure and the desired oxidation resistance will have been achieved.

Two suitable methods for applying the above described concepts will now be readily apparent. In one, the alloy composition may be prepared by melting the molybdenum or molybdenum base alloy in a suitable furnace under a controlled atmosphere to avoid oxidation or contamination of the melt and adding thereto a desired retarder or stabilizer in effective amounts up to 6% by weight and the desired amount of diffusion barrier element in amounts up to 1.0% by weight.

A second method of applying this technique is to coat the molybdenum or molybdenum base article after it has been formed with a mixture of powder in a suitable vehicle compounded so as to contain the proper proportions of retarder and diffusion barrier additives.

When the first method is employed, the desired alloys may be prepared as follows:

The coarsely granular metals (approximately 20 to 40 mesh) are mixed in suitable proportions and compressed into pellets. These pellets are then fused twice in an arc furnace operating in an argon atmosphere at approximately half atmospheric pressure. The arc furnace consists of a water-cooled copper hearth and a water-cooled tungsten tip. The double melting is utilized to insure uniformity. The buttons obtained are rolled into sheet and the edges of the sheet cropped. The analyses given in the table below are those obtained on the finished alloy. The oxidation resistance is determined qualitatively by examination of specimens after a 3-hour exposure in air at 2000° F. and 2500° F.

Suitable alloys for the purpose and an indication of their oxidation resistance are given in the following table.

	Wt. Percent Retarder	Wt. Percent Stabilizer	Wt. Percent Mo	Oxidation Resistance	
				2,000° F.	2,500° F.
1-----	0-----	0-----	100.0	Nil-----	Nil-----
2-----	5.0 Si-----	0-----	95.0	Fair-----	Poor-----
3-----	4.70 Si-----	0.77 La-----	94.5	Excellent--	Good-----
4-----	5.01 Al-----	0.66 Ce-----	94.3	-----do-----	-----Do-----
5-----	5.21 Cr-----	0.95 Ca-----	93.0	-----do-----	-----Do-----
6-----	3.98 Al-----	0.96 Ca-----	95.0	-----do-----	Excellent--
7-----	4.52 Zr-----	0.86 Sn-----	94.6	-----do-----	Fair-----

Having now described my invention in accordance with the patent statutes, I claim:

1. An oxidation resistant molybdenum base alloy consisting of between about 0.5% and 6% by weight of at least one element retarding the oxidation of molybdenum and selected from the group consisting of beryllium, titanium, aluminum, zirconium, chromium, silicon, and vanadium, and between about 0.1% and 1.0% by weight of at least one molybdenum oxide stabilizer from the group consisting of calcium, cerium, erbium, lanthanum, neodymium, praeosodymium, lead and tin, balance essentially all molybdenum.

2. An oxidation resistant molybdenum base alloy consisting of between about 0.5% and 6% by weight of aluminum, between about 0.1% and 1.0% of calcium, balance essentially all molybdenum.

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