

1

2,883,282

PROTECTION OF NIOBIUM FROM OXIDATION

Eugene Wainer, Cleveland Heights, Ohio, assignor to Horizons Incorporated, a corporation of New Jersey

No Drawing. Application May 21, 1957
Serial No. 660,491

4 Claims. (Cl. 75-174)

This invention relates to niobium 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 niobium is protected from destructive oxidation.

More particularly, it relates to alloys of niobium 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 4% 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 0.5% and selected from the group consisting of calcium, cerium, erbium, lanthanum, neodymium, praseodymium, lead, thorium, or tin.

Niobium and niobium 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 niobium or many niobium base alloys are exposed to oxidation at high temperatures, coatings form on the surface ranging from Nb₂O to and including Nb₂O₅. With continued exposure, or with intensive oxidation, the coatings formed become thick and flake off, and thereby expose a fresh surface to further oxidation. As a result, the article is ultimately weakened to the point of failure.

One previously proposed means for overcoming this poor oxidation resistance has been to clad the niobium or niobium base alloy article with a suitable oxidation resistant alloy. This approach has not been entirely successful because diffusion between the cladding material and the niobium 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 niobium and niobium 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 subjected to bending stresses.

One object of this invention is to provide a means for protecting niobium and niobium 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 niobium base material.

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

2

plish 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 niobium 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 niobium, 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 niobium 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 niobium 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 niobium 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 niobium-rich systems such as those presently contemplated in which the niobium content comprises substantially at least 95% by weight of the alloy, this oxide will be niobium monoxide. On continued heating the atoms of the stabilizer or retarder additive or additives diffuse rapidly through the superficial film of niobium oxide 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 niobium oxide lattice maintain the structure and composition of the niobium monoxide 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 niobium oxide is additionally responsible for maintaining the stability of the niobium monoxide 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 niobium to the monoxide and even to the metal and each of the stabilizers listed may be added from effective amounts up to about 4% by weight of a total of the listed elements.

As a result of diffusion of both niobium 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 niobium oxide, and as a result it blocks any

openings that may be available in the niobium oxide structure. As a result, the niobium atoms of the base metal can no longer diffuse through the niobium 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 niobium or niobium 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 4% by weight and the desired amount of diffusion barrier element in amounts up to 0.5% by weight.

A second method of applying this technique is to coat the niobium or niobium 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 Nb	Oxidation Resistance	
				2,000° F.	2,500° F.
1-----	0-----	0-----	100.0	Nil-----	Nil-----
2-----	3.5 Si-----	0-----	96.5	Fair-----	Poor-----
3-----	3.70 Si-----	0.47 La-----	95.5	Excellent-----	Good-----
4-----	3.81 Al-----	0.36 Ca-----	95.4	do-----	Do-----
5-----	4.11 Cr-----	0.76 Ca-----	95.1	do-----	Do-----
6-----	4.05 Zr-----	0.61 Th-----	95.2	do-----	Do-----
7-----	3.91 Al-----	0.51 Ca-----	95.3	do-----	Excellent-----
8-----	3.41 Zr-----	0.81 Sn-----	95.5	do-----	Fair-----

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

1. The method of protecting niobium from destructive oxidation which comprises: forming an alloy consisting essentially of between 0.5% and 4% by weight of at least one element from the group consisting of beryllium, titanium, aluminum, zirconium, chromium, silicon and vanadium and between about 0.1% and 0.5% by weight of at least one element from the group consisting of calcium, cerium, erbium, lanthanum, neodymium, praseodymium, lead, thorium, and tin; balance substantially all niobium.

2. The method of protecting niobium and niobium base alloys from destructive oxidation which comprises: incorporating at least in the region of the outer surface of a member formed of said metals between 0.5% and 4% by weight of at least one element retarding the oxidation of niobium and niobium base alloys and selected from those elements having an atomic volume less than the molecular volume of niobium monoxide and between 0.1% and 0.5% by weight of at least one element serving as barrier to the diffusion of niobium oxide in said alloys and selected from those elements having an atomic volume greater than the molecular volume of niobium monoxide.

3. An oxidation resistant niobium base alloy consisting of between about 0.5% and 4% by weight of at least one element from the group consisting of beryllium, titanium, aluminum, zirconium, chromium, silicon, and vanadium, and between about 0.1% and 0.5% by weight of at least one element from the group consisting of calcium, cerium, erbium, lanthanum, neodymium, praseodymium, lead, thorium and tin, balance essentially all niobium.

4. An oxidation resistant niobium base alloy consisting of between about 0.5% and 4% by weight of aluminum, between about 0.1% and 0.5% of calcium, balance essentially all niobium.

References Cited in the file of this patent

UNITED STATES PATENTS

40 1,167,827 Kaiser ----- Jan. 11, 1916
2,400,255 Pfeil ----- May 14, 1946

FOREIGN PATENTS

45 488,926 Great Britain ----- July 12, 1938

OTHER REFERENCES

United States Atomic Energy Commission (BMI-1003), publication on "Initial Investigation of Niobium and Niobium-Base Alloys," written by Battelle Memorial Institute, Columbus, Ohio, June 23, 1955 (pages 28 and 30).