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OXIDATION RESISTANT COATINGS ON NIOBIUM

Lawrence Sama, Seaford, N.Y., Harry P. Kling, Baltimore, Md., and Harry Bender, Albertson, N.Y., assignors to the United States of America as represented by the United States Atomic Energy Commission

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This invention relates to fabricable, oxidation resistant niobium base alloys suitable for the protection of niobium base core materials, and a method of making the same. Specifically, it relates to aluminum dipping of niobium-titanium alloys with or without ternary additions to produce an article of superior resistance to oxidation at high temperatures.

It is well known that pure niobium has considerable strength at temperatures above the range of usefulness of present nickel and cobalt-base alloys; i.e. 1800° F.–2200° F. However, niobium has no practical use in normal atmospheric environments above about 300° C. because of its relatively rapid rate of oxidation. Because of this, intensive efforts have been made to improve the oxidation resistance of niobium. These efforts have included attempts to coat niobium with enamels or by dipping in aluminum. Such attempts were unsuccessful. Other efforts have been directed to improving oxidation resistance by alloying with other metals, particularly titanium, molybdenum, and vanadium. Ternary additions to titanium-niobium alloys, such as nickel, chromium and aluminum give added improvement. However the alloying additions to niobium give insufficient improvement for extended exposure at or above 1800° F., and in high percentages cause considerable impairment of the fabricability of niobium. In fact, a number of alloys having very high additions of titanium and aluminum were found to be quite oxidation resistant at 2200° F. but were not fabricable at all.

The intermetallic $NbAl_3$ is known to have good high temperature oxidation resistance but is not easily fabricable and has other undesirable physical properties. When pure niobium is aluminum dipped, oxidation resistance is improved by formation of $NbAl_3$ but attempts to produce coats thicker than 0.001" have been unsuccessful and the oxidation resistance obtained in this way is not sufficient for exposure at 1800° F. or above for extended periods.

Prior to this invention, therefore, neither alloying nor aluminum dipping was sufficient to produce a fabricable, oxidation resistance material suitable for the protection of niobium base core materials in the temperature range of 1800° F. to 2200° F.

It is the object of this invention to provide a fabricable alloy having excellent oxidation resistance at 1800° F. and higher by a combination of internal alloying and aluminum coating of niobium.

The foregoing objective is accomplished by alloying niobium with from 20 to 75 atomic percent titanium and then coating with aluminum. The optimum titanium composition is approximately 40 atomic percent. All of the alloys can be easily cold fabricated. Ternary additions of aluminum up to 20 atomic percent give alloys which can also be cold fabricated and have superior resistance to cyclic oxidation. When suitably coated with aluminum and heat treated, these alloys have up to 20,000 times more oxidation resistance than pure niobium at 1800° F. and up to 5000 times more resistance at 2200° F.

The alloy is prepared by vacuum arc-melting, taking special precautions later to check for non-homogeneity. After the alloy has been fabricated to the desired shape

and thickness, all sharp edges and corners should be removed. As the method of coating with aluminum is usually by dipping, a suspension wire or strap of a similar alloy material is spot welded on the alloy article. The surface is further prepared for dipping by sandblasting followed by rinsing in an organic solvent. Coating is accomplished by dipping in an unfluxed molten aluminum bath. Alternatively the alloy can be fluxcoated and dipped in a flux covered aluminum bath. The latter method, however, is less practical and subject to more limitations.

In dipping pure niobium, alloying with the pure aluminum coating cannot be controlled such as is done with iron and steel. At dipping temperatures up to 1800° F. the thickness of the coating is dependent on the viscosity of the aluminum and little alloying is accomplished at the surface. At higher temperatures the bath dissolves the niobium without increasing the amount of aluminum deposited.

The titanium alloying additions afford control over the amount of aluminum deposited and improve the oxidation resistance. By dipping in the range 1600° F.–1700° F.—temperatures much higher than used with steel—at times up to several minutes depending on the alloy, any thickness of aluminum desired can be obtained. For example, approximately 0.002" of aluminum is deposited on a 40 percent titanium alloy in about one minute at 1700° F. With higher titanium or ternary alloy additions the times can be shortened or the temperature lowered to get an equivalent aluminum thickness. It is not known exactly what occurs at the alloy surface, but it is apparent that a relatively soft and ductile two phase layer is formed. The coated article can then be subjected to service conditions, but it is more advantageous to give it a diffusion treatment first. The best method consists in the use of a calorizing mix in an argon atmosphere for about an hour in the temperature range 1800° F.– 2200° F. The resultant surface consists of several layers of different intermetallics, the outermost being highly oxidation resistant. Samples with a 0.0025" thick aluminum coating treated in this way have been subjected to oxidizing conditions at temperatures up to 2300° F. for up to several hundred hours with no deleterious effects.

This invention may be more fully understood by reference to the following specific examples:

ALUMINUM COATED TITANIUM-NIOBIUM ALLOYS

The following niobium-titanium alloys were prepared by vacuum arc-melting and tested:

Table I

Melt	Nominal Composition, a/o in Nb	As melted hardness, D.P.H.	Cold rolled		Reduction thickness, percent
			From, In.	To, In.	
162	10 Ti	157	0.256	0.020	92
163	25 Ti	169	0.272	0.019	92
158	40 Ti	163	0.260	0.020	92
164	75 Ti	138	0.342	0.020	94
171	100 Ti	125	0.400	0.020	95

All of these alloys were ductile. After fabricating samples from these alloys, the samples were prepared for dipping by abrading and cleaning in acetone. Next the samples were held with tongs and pre-fluxed in molten potassium acid fluoride at 200–300° C. One end of the sample was immediately dipped into a molten aluminum bath covered by a commercial aluminum brazing flux.

The pre-fluxing and dipping procedure was repeated to coat the other end of the sample, and residual flux was removed therefrom with dilute acid. The aluminum bath was at a temperature of 1350° F. to 1450° F., samples were immersed for several seconds, and the thickness of the aluminum coating was estimated at 0.003" to 0.007" when the bath temperature was in the range 1400° F. to 1450° F. Higher bath temperatures gave thinner coatings in general.

After subjecting the coated titanium niobium samples to a diffusion treatment in argon, they were given an oxidation test at both 1800° F. and 2200° F. with the results given below. The oxidation test was performed by heating in air, and evaluation of oxidation resistance was made on a weight gain basis.

All of these ternary titanium-aluminum-niobium alloys were amenable to cold rolling. Further investigation in this ternary system with higher aluminum concentrations was undertaken. Two alloys, 40 percent Ti–20 percent Al–40 percent Nb; and 35 percent Ti–30 percent Al–35 percent Nb were prepared to determine the maximum concentration of aluminum that this ternary system could tolerate and maintain its cold ductility. These alloys, however had D.P.H. hardness values of 460 and 329 respectively, which are believed to be too high for cold rolling.

Undipped 40 percent titanium-aluminum-niobium alloys were tested for oxidation resistance with the results given in Table V below.

Table II

WEIGHT GAINS OF VARIOUS REVERSE ALUMINUM-DIPPED MATERIALS OXIDIZED AT 1800° F. IN AIR AFTER DIFFUSION IN ARGON

Sample	Alloy, a/o in Nb	Run No.	Diffusion Treatment	Total Weight Gain—g./cm.²				
				20 hrs.	40 hrs.	60 hrs.	80 hrs.	104 hrs.
162	10 Ti	270-24	2,200° F.—2 hr	0.0232	0.0259	0.0588		
162	10 Ti	270-25	2,200° F.—2 hr	0.0156	0.0255	0.0707		
162	10 Ti	277-46	2,300° F—2 hr	0.0227				
162	10 Ti	277-47	2,400° F.—2 hr	0.0295				
163	25 Ti	277-41	2,200° F—2 hr	0.0027	0.0049	0.0075	0.0228	
163	25 Ti	277-43	2,200° F—16 hr	0.0028	0.0046	0.0057	[1] 0.0097	
163	25 Ti	277-42	2,300° F.—2 hr	0.0030	0.0047	0.0061	0.0116	
172	40 Ti	270-26	2,200° F.—2 hr	0.0008	0.0011	0.0013		0.0027
172	40 Ti	270-27	2,200° F.—2 hr	0.0010	0.0016	0.0019		[1] 0.0051
164	75 Ti	270-23	2,200° F.—2 hr	0.0005	0.0014	0.0017		0.0072
164	75 Ti	270-22	2,200° F.—16 hr	0.0019	0.0029	0.0037		0.0060

[1] Accelerated attack at an end or edge.

Table III

WEIGHT GAINS OF VARIOUS REVERSE ALUMINUM-DIPPED MATERIALS OXIDIZED AT 2200° F. IN AIR AFTER DIFFUSION IN ARGON

Sample	Alloy, a/o in Nb	Run No.	Diffusion Treatment	Total Weight Gain—g./cm.²				
				20 hrs.	40 hrs.	60 hrs.	80 hrs.	128 hrs.
162	10 Ti	269-19	2,200° F.—2 hr	0.0127	0.0761			
162	10 Ti	269-21	2,200° F.—16 hr	0.0588				
162	10 Ti	272-34	2,300° F.—2 hr	0.0741				
162	10 Ti	272-36	2,400° F.—2 hr	0.0526				
162	10 Ti	278-50	2,400° F.—2 hr	0.0749				
158	40 Ti	269-17	2,200° F.—16 hr	0.0027	0.0045	0.0073		[1] 0.0262
172	40 Ti	269-18	2,200° F.—2 hr	0.0036	0.0102	0.0151		
172	40 Ti	278-48	2,300° F.—2 hr	0.0011	0.0020	0.0026	0.0033	0.0501
164	75 Ti	269-20	2,200° F.—2 hr	0.0058	0.0153	0.0256		0.0717
164	75 Ti	269-16	2,200° F.—16 hr	0.0162	0.0349			

[1] Accelerated attack at an edge or end.

Tables II and III show that aluminum coated 40 percent titanium-niobium has better oxidation resistance than other alloys having higher and lower titanium content. With this binary alloy as a base, additions of aluminum up to 15 percent were made to it. These ternary alloys were tested for fabricability, with the results given below:

Table IV

Melt	Composition, a/o in Nb	As-Melted Hardness, D.P.H.	Cold rolled		Reduction in thickness, percent
			From, In.	To, In.	
179	40 Ti-5 Al	227	0.255	0.012	95.0
180	40 Ti-10 Al	251	0.220	0.012	94.5
185	40 Ti-5 Al	219	0.265	0.020	92.5
186	40 Ti-10 Al	250	0.250	0.020	92.0
187	40 Ti-15 Al	272	0.295	0.020	93.0
188	35 Ti-15 Al	281	0.277	0.020	92.5

Table V

WEIGHT GAIN FOR TERNARY NIOBIUM BASE ALLOYS OXIDIZED IN AIR AT 1800° F. AND 2200° F.

Sample	Composition, a/o in Nb	Weight Gain—g./cm.²	
		1,800° F.	2,200° F.
185	40 Ti-5 Al	0.0020—1 hr	0.0137—1 hr.
185	40 Ti-5 Al	0.0327—16 hr	
186	40 Ti-10 Al	0.0014—1 hr	0.0126—1 hr.
186	40 Ti-10 Al	0.159—16 hr	
186 [1]	40 Ti-10 Al	0.0088—16 hr	
187	40 Ti-15 Al	0.0011—1 hr	0.0087—1 hr.
187	40 Ti-15 Al	0.0077—16 hr	
187	40 Ti-15 Al	0.0263—64 hr	
187 [1]	40 Ti-15 Al	0.0308—64 hr	
188	35 Ti-15 Al	0.0016—1 hr	0.0091—1 hr.
188	35 Ti-15 Al	0.0068—16 hr	

[1] Pretreated in argon at 2200° F. for one hour.

Table V shows that weight gains decrease with increasing aluminum content at both 1800° F. and 2200° F. At 1800° F. differences between alloys are more noticeable at the longer time test. The alloys with 15 percent Al had lower weight gains than any ductile alloy made. At 1800° F. these alloys have weight gains of ⅓ to ¼ that of the best ductile binary alloys, and at 2200° F. the weight gains are ½ to ⅓ that of the best ductile binary alloys.

Samples of the ternary titanium-aluminum-niobium alloys of Table V were coated with aluminum. Instead of reverse dipping as practiced with the earlier samples, holes were drilled through the samples, which were then suspended by a wire. The usual KHF_2 flux treatment was used on the samples following which they were dipped in a fluxed aluminum bath for 20 seconds. The resultant coatings were more uniform than those previously obtained, but a small excess of aluminum was picked up around the wire in the hole in the sample. Following a two hour diffusion treatment at 2200° F. in argon, the samples were oxidized for 20 hours at 2200° F. examined, weighed and then oxidized for another 20 hours. The ternary alloy sample 40 percent Ti–15 percent Al–45 percent Nb, when aluminum dipped, had a lower weight gain at 2200° F. than any 40 percent Ti sample tested. After 100 hours at 2200° F. the sample appeared little affected by oxidation. Metallographic measurements indicated less than 0.001 inch of oxide penetration. The comparative weight gain of this alloy with the gain for pure niobium or titanium-niobium binary alloys is shown in Table VI.

Table VI

WEIGHT GAIN DATA FOR ALUMINUM DIPPED PURE NIOBIUM AND NIOBIUM ALLOY SAMPLES OXIDIZED AT 2200° F.[1]

Composition, a/o in Nb	Total Weight Gain—g./cm.[2]				
	Exposure Time—Hours				
	20	40	60	80	100
Nb	0.0832				
Nb	0.0821				
Nb	0.0830				
Nb	0.0831				
10 Ti	[2] 0.0562				
10 Ti	[2] 0.0428				
10 Ti	0.0848				
40 Ti	0.0008	0.0191			
40 Ti	0.0013	[2] 0.0328			
40 Ti	0.0022	[2] 0.0068			
40 Ti	0.0018	0.0130			
40 Ti	[2] 0.0067				
40 Ti	0.0019	[2] 0.0035	0.0078	0.0140	
35 Ti–15 Al	[2] 0.0057				
40 Ti–15 Al	0.0007	0.0015	0.0022	0.0028	0.0035

[1] All samples diffused for two hours at 2,200° F. in argon prior to test
[2] Accelerated attack at an edge or end.

In preparing further samples, prefluxing in potassium acid fluoride preparatory to dipping in a flux covered aluminum bath was abandoned. Instead samples were prepared by acid pickling in strong $HF–HNO_3$ followed by rinsing and drying. Alternatively, the samples were sandblasted and rinsed with an organic solvent.

The thickness of the aluminum coating varies with the niobium alloy and the bath temperature. Coatings 0.002" thick can be obtained by dipping at 1700° F. for one minute. Reactions below 1600° F. bath temperature tend to be too slow; at 1800° F. reactions were too rapid for ready control. Dipping time is variable from about 15 seconds to 120 seconds. Diffusion treatment is preferably conducted at 1900° F. in argon for one hour with a calorizing mix.

The aluminum coated titanium-niobium alloys of this invention offer many advantages. The excellent high temperature strength and nuclear properties of niobium and its alloys can be retained without impairment of fabricability. Almost any shape and size of article can be treated. Alloying with titanium with its poor nuclear properties can be restricted to the surface of the article. A large variety of niobium base materials can be so protected. Coating with the usual high temperature alloys such as nickel base alloys limits service temperatures since a low melting eutectic is formed at 2100° F. Other alloy coatings such as Fecral are less compatible with niobium because of widely varying thermal expansion coefficients and the formation of brittle intermetallics at the clad-niobium interface. In addition the coating provided by this method is plastic enough to deform without spalling off or cracking at test temperatures of 2200° F.

We claim:

1. A fabricable high temperature oxidation resistant alloy for the protection of niobium base core materials that comprises a titanium-niobium alloy consisting of 20–75 atomic percent titanium and the balance niobium, coated with aluminum.

2. An alloy as set forth in claim 1 wherein the titanium-niobium alloy comprises approximately 40 atomic percent titanium and the balance niobium.

3. A fabricable high temperature oxidation resistant alloy for the protection of niobium base core materials that comprises a titanium-aluminum-niobium alloy consisting of 20–75 atomic percent titanium, up to 15 atomic percent aluminum, and the balance niobium, said titanium-aluminum-niobium alloy being coated with aluminum.

4. An alloy as set forth in claim 3 wherein the titanium-aluminum-niobium alloy comprises 40 atomic percent titanium, 15 atomic percent aluminum and the balance niobium.

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DAVID L. RECK, *Primary Examiner.*

WILLIAM G WILES, ROGER L. CAMPBELL, *Examiners.*