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COLUMBIUM BASE ALLOY ARTICLE

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This invention relates to columbium base alloys and, more particularly, to an oxidation resistant coating for columbium base alloy articles.

As the technology in the art of power producing apparatus, such as gas turbines, advances and becomes more complex, there is an ever increasing need for materials which have high strength at the high temperature operating conditions of such complex apparatus coupled with resistance to oxidation. Alloys of the refractory metal columbium have a great potential for structural applications at elevated temperatures, not only because of their high strength-to-weight ratio, but also because of their relatively low rates of oxidation as compared with other fabricable refractory metals and alloys. However, even though the oxidation rates of columbium base alloys are comparatively low, they still oxidize at the rate of 2 to 3 times greater than acceptable values. Hence, surface protection of these alloys is mandatory for practical applications.

One method of increasing oxidation resistance is to diffuse into the surface of columbium base alloys certain alloying elements, such as aluminum, so that through the subsequent formation of stable compounds, oxidation resistance is imparted to the alloy.

Coatings of aluminum have been known to increase the oxidation resistance of iron, copper, cobalt and nickel base alloys. Application methods include dipping into molten aluminum or aluminum alloy baths, spraying on molten aluminum, flame depositing semimolten aluminum or its alloys, vapor deposition and the like.

Aluminum alloys suitable for use as coating materials have been reported to include small additions of Be, Ce, Cr, Cu, Co, Mg, Mo, Si, Ti, V and Zn all of which are said to impart increased oxidation resistance to the coated article.

A principal object of this invention is to provide a columbium base alloy article of improved oxidation resistance, imparted thereto through a unique aluminum base alloy coating.

This and other objects and advantages will become more apparent from the following detailed description which is meant to be exemplary rather than a limitation on the broad scope of the present invention.

It has been found that in order to impart improved oxidation resistance to a columbium base alloy article, the columbium base alloy itself, prior to manufacture into an article, should be first alloyed with between 1–10% by weight titanium. Therefore, in one form, the present invention provides an improved oxidation resistant columbium base alloy article including between 1–10% titanium and coated with an aluminum base alloy comprising 5–15% by weight silicon with the balance aluminum. In another form, this invention provides an improved oxidation resistant columbium base alloy article coated with an aluminum base alloy comprising 1–10% by weight titanium, 5–15% by weight silicon with the balance aluminum.

The preferred method by which the article of this invention is made is through the use of a molten aluminum alloy bath into which the article can be dipped, although it is contemplated that such aluminum alloy coating can be applied by the many deposition processes well known in the art. These include but are not limited to spraying of molten metal, spraying of powder coupled with further heat treatment, vapor deposition, electrodeposition followed by heat treatment, etc.

Molten aluminum and molten aluminum alloy baths are well known as a method of imparting oxidation resistance to various materials. The inclusion of silicon within the range of 5–15% by weight similarly are well known in this art. However, additions to such Si—Al alloys such as Be, Ce, Cr, Cu, Co, Mg, Mo, Si, Ti, V and Zn do not always result in improved oxidation resistance when applied to columbium base alloys, and have been shown not to be equivalents.

It had been recognized that an aluminum base alloy including about 15% by weight silicon imparted the best oxidation resistance to a columbium base alloy including nominally about 10% by weight titanium. In order to determine and evaluate dipping and post-treatment parameters on the 2300° F. oxidation resistance of such a titanium bearing columbium alloy, 15 centerless ground 0.353" diameter by ½" long samples were ground from an arc melted columbium base alloy after extrusion and consisting essentially in percent by weight of 6.8% Ti, 6.35% Mo, 0.34% Zr, with the balance Cb. The surface of the sample was first activated by vapor blasting and was then washed with water. The samples were then dipped in a 15% Si, balance Al alloy which had been pre-alloyed in an argon atmosphere induction furnace and re-melted in a graphite crucible under a nitrogen blanket. The remelted aluminum alloy was covered with a standard commercial fluoride-containing brazing flux (Alcoa #30). The samples were dipped from one to thirteen minutes at a temperature of 1500–1900° F. after which they were removed from the molten aluminum and excess aluminum was removed by vigorously shaking the samples. After the dipping operation, the samples were heat treated at 1700–2100° F. for one hour in argon. The samples were then oxidized in static, ambient air for twenty-four hours at 2300° F. The results of this testing indicated that an optimum dipping time and temperature and post-treatment was about three minutes at about 1700° F. and a post-treatment in vacuum for about one hour at about 1900° F. This same series of tests was repeated on samples of alloys A, B, C, and D of Table I below as well as on unalloyed columbium for one, two and three minutes. It was shown that an optimum oxidation resistance condition for a minimum coating thickness (10 mils) can be attained by a three minute dip at 1700° F. with a post-treatment in vacuum for one hour at about 1900° F., although it was recognized that slightly greater oxidation resistance can be obtained by dipping for longer times and/or higher temperatures to obtain greater coating thicknesses.

In order to determine the effects of the number of variables on the oxidation resistance of columbium and columbium alloys, a number of aluminum alloys were applied to a number of columbium base alloys. Included in the following Table I are examples of typical columbium base alloys to which various aluminum base alloys were applied.

TABLE I

Cb alloy	Percent by weight					
	W	Mo	Ta	Zr	Ti	Cb
A	----	----	33	0.75	0	Balance.
B	15	5	----	1	0	Do.
C	15	5	----	1	5	Do.
D	----	----	----	----	8	Do.

Samples of the above listed columbium base alloys were used in the form of sheets about ½" square. These samples were prepared in a manner the same as described above prior to the aluminum alloy dip. The samples were than dipped at 1700° F. for three minutes under an argon protective atmosphere in the aluminum alloys listed in Table II.

TABLE II

Al alloy	Percent by weight			
	Si	Ti	Cu	Mg
1	25			
2	15	10		
3	15	5		
4	15		10	
5	15		5	
6	0			10
7	15			10
8	15			5

The difficulty was encountered by the inability of the aluminum alloys containing magnesium to uniformly coat the samples; further study on the alloys containing magnesium was discontinued.

Immediately after withdrawing the dipped samples from the bath, the excess aluminum alloy was removed by vigorously shaking. Following the dipping operation the samples were post-treated at 1900° F. for one hour. All samples were initially weighed separately and then oxidized for twenty-four hours at 2300° F. in static, ambient air. The samples were removed from the furnace and weighed after two, four and twenty-four hours. The weight gain in mg./cm.^{2} vs. time of exposure at 2300° F. is given in the following Table III.

TABLE III

Oxidation Test at 2300° F.

Cb alloy	Al alloy	Weight gain (mg./cm.^{2})		
		2 hours	4 hours	24 hours
A (0 Ti)	2 (10 Ti)	5.5	7.9	13.9
	5 (5 Cu)	96.5	(1)	(1)
	4 (10 Cu)	38.2	100.8	(1)
B (0 Ti)	1 (0 Ti)	6.4	14.6	177.5
	3 (5 Ti)	4.9	7.0	11.1
	2 (10 Ti)	10.0	15.2	22.4
	5 (5 Cu)	47.3	108.9	267.0
	4 (10 Cu)	48.6	169.0	(1)
C (5 Ti)	1 (0 Ti)	5.5	12.0	140.1
	3 (5 Ti)	4.9	5.7	7.7
	2 (10 Ti)	6.0	7.8	23.3
	5 (5 Cu)	39.5	54.4	175.8
	4 (10 Cu)	42.5	93.8	222.5
D (8 Ti)	1 (0 Ti)	1.3	3.4	48.5
	3 (5 Ti)	4.4	6.6	10.7
	2 (10 Ti)	4.9	15.1	36.2
	5 (5 Cu)	10.7	35.6	123.0
	4 (10 Cu)	11.0	35.3	(1)

[1] Completely oxidized.

As was mentioned above the optimum post-treatment was for one hour at about 1900° F. in vacuum. In the vacuum post-treatments, the specimens were mounted on a piece of molybdenum mesh and supported by tantalum wire. A vacuum of 0.02 micron was obtained in the furnace in which the samples were treated. At the completion of the testing the samples were removed from the heated portion of the furnace and allowed to cool in vacuum, in this case for one hour, before opening to the atmosphere.

Referring now to Table III above it can be easily seen that the inclusion of up to about 10% by weight titanium in the aluminum coating alloy or the inclusion of titanium in the columbium alloy alone or in combination with titanium in the aluminum coating alloy results in a system affording significantly improved oxidation resistance as compared with such alloys or such coatings not including titanium up to about 10% by weight. It is readily observed that the copper bearing aluminum coating alloys were very detrimental. Referring to columbium alloy B in which no titanium is included, it can be observed in Table III that the addition of 5–10% titanium in the coating alloy significantly improves the long time oxidation resistance although it is apparent from the comparison of aluminum alloy coating 3 with 2 when applied to columbium alloys B, C and D that an optimum value of titanium in the coating is in the range somewhat less than 10% by weight. Referring to columbium alloy D including 8% by weight titanium and coated with aluminum coating alloy 1 including no titanium, an improved oxidation resistance is obtained over columbium base alloys not including titanium although the addition of small amounts of titanium up to about 10% by weight improves the oxidation resistance of such alloys.

Therefore, although aluminum alloy coatings for oxidation resistance which may include 5–15% by weight silicon and a number of other addition elements will impart an oxidation resistance to a number of varieties of alloys such as those based on iron, nickel, cobalt and the like, this has not been found to be necessarily true for columbium base alloys. This invention in one form recognizes that an unexpected improvement in oxidation resistance can be achieved by the addition of up to about 10% titanium in an aluminum coating bath including 5–15% silicon.

In addition to the optimum method for coating and treating columbium alloys as has been described above it has been found that activating the surface such as by vapor blasting prior to application of the aluminum alloy coating such as through dipping is very significant. For example referring to Table III above, columbium alloy A which had been dipped into a molten bath of aluminum 2 without prior vapor blasting of the surface of the sample resulted in a weight gain after two hours of 8.6, after four hours of 12.6 and after twenty-four hours of 84.7 all of which are significantly greater than the vapor blasted sample of Table III.

Although this invention has been described in connection with specific examples, these examples are meant to be illustrative of rather than limitations on the broad scope of the invention.

What is claimed is:

1. A columbium base alloy article of improved oxidation resistance having a coating of an aluminum alloy consisting essentially of, in percent by weight, about 5–15% Si, 1–10% Ti with the balance aluminum.

2. A columbium base alloy article of improved oxidation resistance having a coating of an aluminum alloy consisting essentially of, in percent by weight, about 5–15% Si, 1–5% Ti with the balance aluminum.

3. A columbium base alloy article of improved oxidation resistance having a coating of an aluminum alloy consisting essentially of, in percent by weight, about 5–15% Si, about 5% Ti with the balance aluminum.

4. A columbium base alloy article including from a small amount up to about 10% by weight titanium of improved oxidation resistance having a coating of an aluminum alloy consisting essentially of, in percent by weight, about 5–15% Si, 1–10% Ti with the balance aluminum.

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