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OXIDATION RESISTANT COATINGS FOR COLUMB-
BIUM AND COLUMBIUM ALLOYS
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The present invention relates to protective coatings for
columbium and its alloys, and in particular to tin base
alloy coatings for protecting columbium and its alloys
against oxidation in air at temperatures in the range of
1100° F. to 1800° F.
Previously it was found that columbium base alloys
containing 30-40 atomic percent titanium could be pro-
tected for 500-1000 hours at 1800° F. by hot dipping in
aluminum base alloys, such as Al-10 Cr and Al-11 Si.
However, alloys with high titanium compositions are un-
desirable for high temperature applications because of
their inferior characteristics at such temperatures.
It was also known that low titanium alloys could be
protected for at least 500 hours at 2300° F. by hot dip-

Prior to the present invention an alloy 94 w/o Cb-
5 w/o Mo-1 w/o Ti, dipped in 71 w/o Al-15 w/o Cr-9
w/o Si-5 w/o Sn, had exhibited excellent oxidation resis-
tance for more than 500 hours at 2300° F. Since this
alloy was one of the alloys of particular interest, it was
thought to be a relatively simple matter to produce the
desired coating for service at the lower temperatures of
1100° F. to 1800° F. A series of tests were accordingly
instituted to study the oxidation resistance of the conven-
tional Al-11 w/o Si and Al-15 w/o Cr-9 w/o Si-5
w/o Sn dip coatings on various columbium alloys in the
temperature range of 1100° F. to 1800° F. The samples
tested included the Cb-5 w/o Mo-1 w/o Ti alloy just
mentioned, together with Cb-1 w/o Zr and Cb-5 w/o
Mo-2 w/o Ti-2 w/o Zr of particular interest in this in-
vestigation.

Contrary to expectations, it was found that no sample
exhibited the expected resistance. The Cb-5 w/o Mo-1
w/o Ti dipped in Al-15 w/o Cr-9 w/o Si-5 w/o Sn which
had withstood over 500 hours at 2300° F. failed after only
50 to 100 hours at 1100°, 1400° and 1800° F. The other
columbium alloys likewise failed prematurely as shown
by typical data summarized in Tables 1 and 2.

Table 1.—Al-11 w/o Si DIP OXIDATION TEST DATA (HOURS TO FAILURE)

Base alloy	Coating thickness	Temperatures		
		1100° F.	1400° F.	1800° F.
Cb-5 w/o Mo-1 w/o Ti.....	0.002.....	24 hours, white oxide. 192 hrs., surface oxide (white powder), edges ragged.	White oxide formed immediately. 312 hrs., surface oxidized, white powder. Edge failure.	144 hrs., very thick adherent white oxide all over except edges which are eroded.
Cb-1 w/o Zr.....	0.002.....	72 hrs., edges eroded, white oxide on surface.	72 hrs., samples destroyed.....	72 hrs., samples destroyed.
Cb-5 w/o Mo-2 w/o Ti-2 w/o Zr.....	0.002.....	144 hrs., white powder oxide on surface.	48 hrs., white powder oxide on surface, under surface not bad.	144 hrs., very thick adherent white oxide all over except edges which are eroded.

Table 2.—Al-15 w/o Cr-9 w/o Si-5 w/o Sn DIP OXIDATION TEST DATA (HOURS TO FAILURE)

Base alloy	Coating thickness	Temperatures		
		1100° F.	1400° F.	1800° F.
Cb-5 w/o Mo-1 w/o Ti.....	0.002.....	144 hours, coating peeling off, edges eroded.	288 hrs., coating peeling off, edges eroded.	288 hrs., edge failures, surface good.
Cb-1 w/o Zr.....	0.002.....	24 hrs., edge failures, surface OK.	24 a; 120 b hrs., edge failures, surface good.	23 a, 144 b hrs., edge failures, surface good.
Cb-5 w/o Mo-2 w/o Ti-2 w/o Zr.....	0.002.....	120 hrs., coating peeling back from edges.	552 hrs., coating slightly oxidized, edge failure 1 sample.	216 a, 288 b hrs., edge failures, surface good.

a Hours to failure, first sample. b Hours to failure, second sample.

ping in aluminum and certain aluminum base alloys such
as Al-11 Si. These coatings, however, were found not
to afford protection at lower temperatures in the range
of 1100° F. to 1800° F.
It is the object of this invention to provide a coating
for columbium and columbium base alloys that will with-
stand oxidation in air for 500 to 1000 hours in the tem-
perature range of 1100° F. to 1800° F.
It is a specific object of this invention to provide a pro-
tective coating for the alloys: 99 w/o Cb-1 w/o Zr; 94
w/o Cb-5 w/o Mo-1 w/o Ti and 91 w/o Cb-5 w/o
Mo-2 w/o Zr-2 w/o Ti in the temperature range from
1100° F. to 1800° F.
The foregoing objects are achieved by providing a pro-
tective coating consisting mainly of aluminum inter-
metallic compounds on the columbium or columbium
alloys. The coating may be applied by contacting the
columbium with tin containing minor amounts of alumi-
num and zinc at an elevated temperature. Advantage-
ously, the coated columbium may then be given a dif-
fusion treatment at a temperature of about 1900° F. to
dissolve excess tin.

Results comparable to those in Tables 1 and 2 were
obtained when using a dipping bath of pure aluminum
and a bath of Al-5 w/o Cr.
The foregoing studies demonstrated the failure of alu-
minum base coating baths to establish the necessary pro-
tective coating on columbium and columbium containing
minor amounts of alloying elements for service in the de-
sired temperature range. Further work with aluminum
base baths was therefore abandoned.
The present invention resides in the discovery that pro-
tective coatings can be derived by contacting the colum-
bium or columbium alloy with a bath containing a major
percentage of tin, a minor amount of aluminum, and
further additives selected from the class consisting of
zinc, iron, chromium and titanium. Two baths found
to be especially effective are composed respectively of
85 w/o Sn-10 w/o Al-5 w/o Zn and 88.5 w/o Sn-10
w/o Al-1 w/o Cr-0.5 w/o Ti. Dipping temperatures
of 1300° F. to 1950° F. and dipping periods varying
from 2 minutes to over one hour may be used. Prefer-
ably a sodium borate flux is used to clean the surface
of the bath. Test data summerized in the following

Table 3, shows successful performance of the coatings at 1100° F. and 1400° F. in air.

TABLE 3.—OXIDATION TEST RESULTS OF COLUMBIUM ALLOYS DIPPED IN Sn-10 W/O Al-5 W/O Zn. ALL SAMPLES TESTED IN THE AS-DIPPED CONDITION

Base alloy	Run No.	Sample No.	Time to failure (hrs.) at—	
			1100° F.	1400° F.
Cb-----	1	2	596-----	864.
		3	1,484-----	1,104.
		1	216-----	760.
Cb-1 Zr-----	1	2	250-----	984.
		3	480-----	1,400 NF.
		1	168-----	1,000 NF.
	2	2	456-----	1,000 NF.
		3	650-----	1,000 NF.
		1	1,944-----	1,700 NF.
Cb-5 Mo-1 Ti-----	1	2	1,944-----	1,700 NF.
		3	2,130-----	1,700 NF.
		1	500-----	1,000 NF.
	2	2	1,000 NF-----	1,000 NF.
		3	1,000 NF-----	1,000 NF.
		1	1,000 NF-----	1,000 NF.
Cb-5 Mo-2 Ti-2 Zr-----	1	2	1,000 NF-----	1,000 NF.
		3	1,000 NF-----	1,000 NF.
		1	451-----	1,000 NF.
	2	2	500-----	1,000 NF.
		3	1,000 NF-----	1,000 NF.

NF—No failure.

Successful oxidation resistance at 1100° F. and 1400° F. having been achieved as demonstrated by the results tabulated in Table 3, experiments were conducted to determine the oxidation resistance at 1800° F. Both the 85 Sn-10 Al-5 Zn dip used in Table 3, and additional coating baths contained a major proportion of tin were used. In all cases listed in the Table 4, infra, the samples were prepared by sandblasting with steel grit. Dipping was done at a temperature of about 1780° F. for periods of about 8 to 10 minutes. A sodium borate flux was used with all of the baths.

TABLE 4.—TEST RESULTS ON TIN-BASED COATINGS

Coating alloy	Base alloy	Time (hrs.) to Failure at 1800° F.		
		Sample No.		
		1	2	3
88.5 Sn, 10 Al, 1 Cr, 0.5 Ti Dip-----	(Cb-1 Zr (Melt II)-----	550-----	616-----	660.
	Cb-1 Zr (Melt I)-----	500-----	540-----	836.
	Cb-5 Mo-2 Ti-2 Zr (Melt II)-----	891-----	SIT after 900 hrs*	
	Cb-5 Mo-2 Ti-2 Zr (Melt I)-----	1,100-----	1,100-----	SIT after 1,100 hrs.
	Cb (Melt I)-----	484-----	616-----	792.
85 Sn, 10 Al, 5 Zn Dip-----	Cb (Melt II)-----	308-----	396-----	550.
	Cb-5 Mo-2 Ti-2 Zr (Melt I)-----	748-----	800-----	SIT after 800 hrs.
	Cb-5 Mo-2 Ti-2 Zr (Melt II)-----	572-----	SIT after 900 hrs-----	SIT after 800 hrs.
	Cb-1 Zr (Melt II)-----	286-----	287-----	396.
	Cb-----	SIT after 620 hrs-----	SIT after 620 hrs-----	
83 Sn, 10 Al, 5 Zn, 2 Fe Dip-----	Cb-5 Mo-2 Ti-2 Zr-----	330-----	462-----	

*SIT—Still in test.

The unique feature of the coatings is the addition of aluminum, and aluminum-zinc to the tin dipping bath. Resultant coatings consist mainly of aluminum intermetallic compounds which are oxidation resistant to temperatures as high as 2300° F. for long periods of time. Electron probe data of a Cb-5 Mo-1 Ti sample dipped in Sn-10 w/o Al-5 w/o Zn and oxidation tested at 14° F. for over 2000 hours indicated that the phase Cb Al was formed, modified by titanium and molybdenum. The addition of aluminum to the dipping bath has the further important property of a wetting agent. While tin will not wet the columbium, at least at temperatures up to 2000° F., the addition of a few percent aluminum to the bath causes wetting to occur.

We have found that coatings of intermetallics of significant thickness can be obtained at relatively low aluminum, silicon, chromium and zinc concentrations; as low as a total of 5 percent. The coatings can be applied from 1300° F. to 1950° F. for 2 minutes to an hour or

more, and thicknesses up to 0.005" can be obtained. Dipping at 1700° F. to 1900° F. has been found to be especially satisfactory.

Although columbium and its alloys are protected by the dip coatings of this invention, further advantages may be secured by a diffusion treatment to dissolve excess tin from the coating. A diffusion treatment at 1900° F. for one hour has been found to be satisfactory. As a result of this treatment, excess tin disappears with time at temperature.

Experiments have shown that tin is a necessary component of the bath, and that although pure zinc will form a protective intermetallic coating on columbium, a bath composed of aluminum and zinc without tin will not produce as protective a coating in the temperature range of interest.

It is not known why the tin base baths form superior aluminide intermetallics, but it is believed that excess tin contributes to the improved behavior of the coating by acting as a reservoir for repairing defects in the coating in the initial testing stages.

From the foregoing description it is seen that this invention provides oxidation resistant coatings in the temperature range 1100° F. to 1800° F. by dipping columbium and its alloys in a bath of tin containing aluminum and minor amounts of additional elements. By means of these coatings columbium and columbium-rich alloys having superior high temperature strength can be now used in oxidizing environments for prolonged periods.

What is claimed is:

1. The method of protectively coating columbium and columbium base alloys against oxidation in air at temperatures in the range 1100° F. to 1800° F. that comprises cleaning the surface of the columbium, dipping the cleaned columbium for a period of between two minutes to one hour in a molten bath consisting of at least 83 w/o tin, 10 w/o aluminum and the balance selected

from the group consisting of zinc, iron, chromium and titanium, said bath being maintained at a temperature between about 1300° F. and 1900° F. to coat the columbium, and then removing the coated columbium from the said bath.

2. The method of claim 1 wherein the columbium alloy consists of 99 w/o columbium-1 w/o zirconium.

3. The method of claim 1 wherein the columbium alloy consists of 94 w/o columbium-5 w/o molybdenum-1 w/o titanium.

4. The method of claim 1 wherein the columbium alloy consists of 91 w/o columbium-5 w/o molybdenum-2 w/o titanium and 2 w/o zirconium.

5. The method of claim 1 wherein the coating bath consists of 85 w/o tin-10 w/o aluminum and 5 w/o zinc.

6. The method of claim 1 wherein the coating bath consists of 88.5 w/o tin-10 w/o aluminum-1 w/o chromium and 0.5 w/o titanium.

7. The method of claim 1 wherein the coating bath

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consists of 83 w/o tin-10 w/o aluminum-5 w/o zinc and 2 w/o iron.

8. The method of protectively coating the alloy consisting of columbium-5 w/o molybdenum-2 w/o titanium-2 w/o zirconium against oxidation in air at temperatures in the range 1100° F.-1800° F. that consists in sandblasting the alloy with steel grit to prepare the alloy surface for coating, dipping the alloy in a bath consisting of 85 w/o tin- 10 w/o aluminum-5 w/o zinc maintained at a temperature of approximately 1780° F. for a period of approximately 8-10 minutes, and then removing the coated alloy.

9. The method of protectively coating the alloy con-

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sisting of 99 w/o columbium-1 w/o zirconium against oxidation in air at temperatures in the range 1100° F. to 1800° F. that consists in sandblasting the alloy with steel grit to prepare the surface of the alloy for coating dipping the alloy in a bath consisting of 85 w/o tin-10 w/o aluminum-5 w/o zinc maintained at a temperature of approximately 1780° F. for a period of 8-10 minutes, and then removing the coated alloy from the said bath.

No references cited.

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