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PROTECTIVE COATINGS FOR COLUMBIUM AND ITS ALLOYS

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Fig. 2

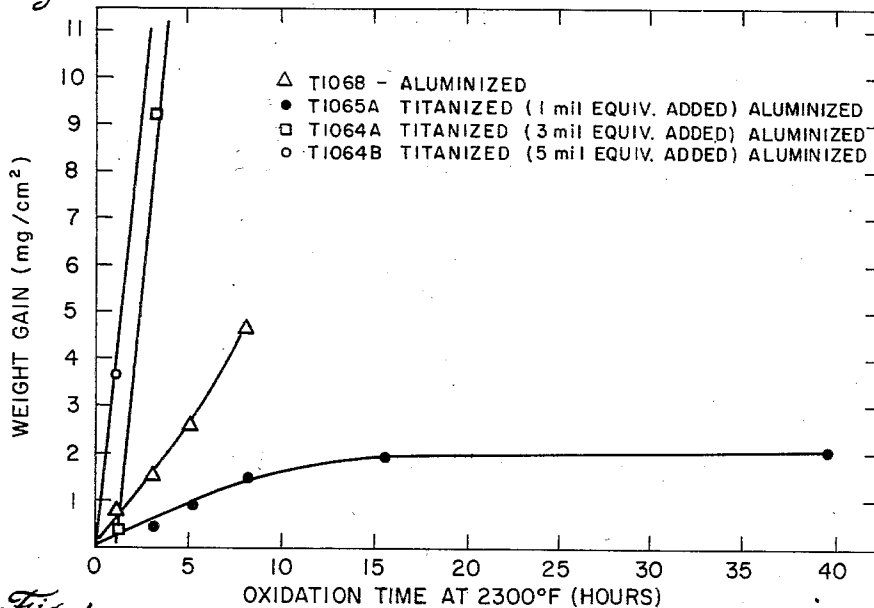
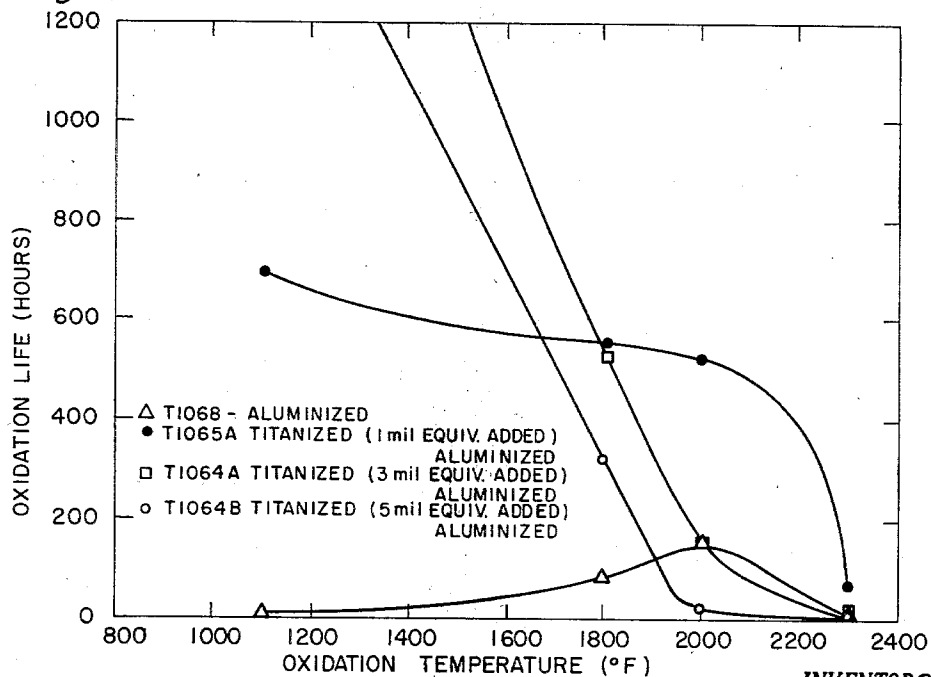


Fig. 1



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PROTECTIVE COATINGS FOR COLUMBIUM AND ITS ALLOYS

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The present invention relates to a new and improved method of protectively coating columbium and its alloys, and is particularly directed to a process for conferring oxidation resistance at temperatures in the range of 1100° F. to 1800° F.

It has been known for a long time that columbium is a most promising metal for nuclear applications because of its low neutron cross section, its high melting point, and its high hot strength. Additionally, columbium is resistant to attack by certain liquid metals, such as lithium, and has good mechanical properties at high temperatures. However both columbium and its alloys are seriously deficient in oxidation resistance. This deficiency has to a large extent been corrected for high temperature oxidation resistance by coating with aluminum and aluminum alloys, principally by hot dipping. Columbium and its alloys coated by such methods, successfully passed hot air tests at 2200° F. for 100 hours.

It was found that aluminum base coatings on columbium, although successful in conferring oxidation resistance at high temperatures such as 2200° F., were prone to oxidation failure at 1100° F. to 1800° F. Although a completely definitive theory has not been presented to explain the poor low temperature oxidation resistance of aluminum base coatings on columbium base alloys, a general understanding of the mechanism has evolved.

Micro-examination of the surfaces of aluminum coated columbium alloys has invariably revealed the existence of many fine hairline cracks which may form a network over the entire surface. After oxidation at a relatively low temperature (1100° F. or 1400° F.) for a relatively short period of time (5-100 hours), it is noticed that an oxidation product will rise in these cracks and/or that pieces of the coating will be lifted off by oxidation occurring in the substrate parallel to the coating surface. In the case where the base metal is moderately oxidation resistant, such as Cb-15 w/o Ti, this process may continue until the coating is completely removed from the sample. In those cases where the base metal itself has poor oxidation resistance, such as Cb-1 w/o Zr, the base metal itself will be destroyed in a short time after the loss of the protective coating.

It is believed that the major factors contributing to oxidation failure at low temperatures are the lack of ductility of the coating at low temperatures and the highly stressed condition of the coating at low temperature. When the coating is formed in a dipping bath at a temperature of 1600° F. or above or during subsequent diffusion treatment at 1900° F., both the coating and the alloy are unstressed. When the sample is cooled down, however, the aluminum base coatings, which have a much greater linear thermal expansion coefficient than any of the columbium base alloys, will tend to contract more than the base metal. Therefore, at any temperature below that at which the coating is formed, the coating will be in tension and the base metal will be in compression.

It has been observed that aluminum base coatings on columbium alloys are cracked during processing, and this is quite understandable since under static conditions the coating is most highly stressed and less ductile at

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ambient temperatures. However, during testing, the sample is subjected to a stress cycle coincident with each thermal cycle. It is reasonable to assume that this may result in the initiation of cracks as well as the propagation of existing cracks.

It is believed that the good performance of aluminum dip coatings at high temperatures results from the stressed condition of the coating. At any temperature above that at which the coating was formed, the coating will be in compression. Hence existing cracks in the coating will be held tightly closed to the extent that oxidation at the base of these cracks will tend to plug them up and prevent further oxidation. Contributing factors are the improved ductility of the coating and improved fusibility of the oxidation products at these higher temperatures.

It is the object of this invention to provide a process of coating columbium and its alloys which will confer oxidation resistance at low temperatures (1100° F.-1800° F.). This object is achieved by depositing a coating of titanium of predetermined thickness on the columbium or columbium alloy base material, and then applying a coating of aluminum, preferably by means of pack calorizing. It has been found that the thickness of the titanium layer is of significant importance to the oxidation behavior of the coated article. For low temperature oxidation resistance a relatively thick layer of titanium, up to 5 mils, produces optimum results. However, for best results at temperatures of 1600° F. to about 2000° F., a relatively thin, 1 mil, layer of titanium is used. The optimum process, therefore, depends upon the conditions of temperature which will be met in actual use of the coated article.

The invention may be more fully understood by reference to the drawings wherein

FIG. 1 is a chart of the oxidation life against temperature of samples of titanized-aluminized Cb-5 w/o Mo-2 w/o Ti-2 w/o Zr;

FIG. 2 is a chart of oxidation life against titanized zone thickness of titanized-aluminized Cb-5 w/o Mo-2 w/o Ti-2 w/o Zr.

The coating is produced by first cleaning the surface of the columbium or columbium alloy article, such as by blasting with steel grit. The cleaned article is then placed in a columbium container in the presence of as-produced titanium sponge, evacuated and heated to a temperature of about 1880° F. to 2400° F. to deposit a titanium rich layer on the columbium article. The length of time and the temperature used control the thickness of the deposit. For example, a deposit of 1 mil thickness can be made by titanizing at 2200° F. for 16 hours. Longer times and higher temperatures produce thicker deposits. After the columbium article has been titanized, an aluminide coating is applied either by hot dipping or pack calorizing. The former method is difficult to apply since the aluminide layer grows rapidly on the high titanium (40 a/o-85 a/o Ti) surface. The resulting thick aluminide cracks severely on cooling. Pack calorizing is thus preferred. The steps of this process are described in more detail as follows:

TITANIZING

After preliminary cleaning, samples of columbium and columbium alloys were packed in a columbium can with as-received titanium sponge. The can was closed with a loosely fitting cover and heated in a vacuum for 16 hours at 2200° F. As a result of this treatment the sponge was slightly fused into one mass but was readily broken apart and the samples removed. There was some slight sticking of titanium particles to the samples, but these were easily picked off except for some extremely fine particles which were fused to the surface. The latter were clean

and finely crystalline. The weight gain indicated a pick-up of 0.0012 inch of titanium. Metallographically an alloy zone 0.0022 inch thick was observed which corresponds to an average composition of Cb-40 w/o Ti. Analysis of the surface by X-ray spectrography confirmed the composition to be as calculated. Deposition of titanium is understood to be due to reaction between columbium and titanium chloride vapors, since titanium sponge is prepared by the reduction of $TiCl_4$ with Mg, and some residual chlorides are always present. Titanium sponge can be reused provided a volatile halide such as NaCl, NH_4Cl or NaF is added to replace the chlorides present in the as-received titanium sponge.

The thickness of the titanium deposit varies somewhat according to the composition of the columbium article, as shown from the following table. In each case the titanizing was continued for 16 hours in a vacuum and at a temperature of 2200° F.

Table I
EFFECT OF BASE ALLOY ON PICKUP DURING
TITANIZING

Base alloy:	Titanium pickup
Cb-5 w/o Mo-2 w/o Ti-2 w/o Zr	mil (standard)---
Cb-1 w/o Zr -----	percent standard--
Cb -----	do-----
Cb-6.25 w/o Ti -----	do-----
Cb-5 w/o Mo-2 w/o Ti-2 w/o Zr with 1	mil titanized layer -----
	do-----

Alternatively, the samples may be suspended out of contact with the titanium sponge. This eliminates the presence of small particles of titanium sintered to the sample surface, previously mentioned, but requires an increase in temperature to 2400° F. to achieve a comparable thickness of titanium.

Thicker coatings of titanium can be obtained by use of a closely fitting cover which prevents escape of volatile titanium halides. This is accomplished by machining square the columbium can and covering it with a weighted sheet of columbium. This assembly is placed in a vacuum furnace, evacuated and brought to temperature. During the process titanium is deposited at the junction of can and cover effecting a seal and preventing further escape of volatile halides. By this method as much as 8½ mils of titanium can be deposited at 2200° F. in 16 hours as compared with 1 mil when an unsealed can was used. At 1850° F. and 16 hours, approximately 4-5 mils are deposited on samples in intimate contact with titanium sponge and 1.3-1.4 mils on samples suspended above the sponge. It should be noted that the packs must be outgassed before the can becomes sealed if satisfactory deposits are to be obtained. Hence the cans should not be sealed before the heating begins.

When the titanizing is performed at lower temperatures, e.g., 1850° F., there is less diffusion of the titanium into the sample. Hence the average composition of the surface layer, as calculated from weight gain and metallographic measurements, is comparatively richer in titanium, amounting to about 60-70 a/o Ti.

The foregoing method successfully coats small, intricate parts, for example screw threads, with a continuous, controlled coating of titanium.

ALUMINIZING

After the sample has been titanized, it is aluminized by coating with aluminum or an aluminum alloy. Dip coating in an aluminum or aluminum alloy bath may be used. However, it has been found extremely difficult to produce thin coatings in this way. It was noticed, for example, that titanized columbium alloys behave differently from Cb-25 w/o Ti alloys that have heretofore been successfully dip coated. When thin coatings were

produced by resorting to very short dip times, the resulting coatings were observed to develop a network of severe cracks during diffusion treatment of the sample after dipping. Also, dip coating is less satisfactory for coating large or intricate shapes than coating by pack calorizing. Hence the latter method is preferred.

Pack calorized coatings were formed on the samples by placing them in stainless steel boats and covering them with a mix consisting of 10-60 w/o metal powder, a 2 w/o carrier such as ammonium chloride (NH_4Cl) and the balance alumina. The metal powder may consist entirely of aluminum or a mixture of aluminum powder and chromium or silicon, or a combination of both chromium and silicon.

Calorizing is performed in argon at temperatures varying from 1300° F. to 1900° F. for periods of 1-4 hours, after which the samples are given a water rinse.

Metal powders consisting of aluminum, Al-10 w/o Cr; Al-11 w/o Si and Al-10 Si-10 Cr have all been successfully employed in calorizing titanized columbium. It was observed that chromium and silicon additions, separately or in combinations, appeared to improve slightly the oxidation life of the resultant coating. At the same time the chromium and/or silicon additions resulted in lesser weight gains during coating, seemingly indicating that these metals are not as readily deposited as aluminum under the processing conditions established. It is therefore assumed that the ratio of alloying elements to aluminum present in the coating is less than the same ratio for the pack mix.

Despite differences in thickness of the Al-Cr, Al-Si and Al-Si-Cr coatings practically identical oxidation resistance was obtained. The significant factor is therefore the thickness of the titanium coating on the life of the sample. The composition of the titanized zones varies with the thickness and titanizing temperatures, and the composition of the titanized surface affects the resultant coating structure. For example, aluminum coatings over surfaces rich in titanium (80 a/o Ti) may be transformed during oxidation to a (Ti, Cb) Al structure from a (Cb, Ti) Al_3 structure, which is typical of coated columbium alloys. The specific effect of the thickness of the titanium coating was therefore studied using a standardized aluminizing treatment consisting of 40% (Al-10 Cr)-2% NH_4Cl -58% Al_2O_3 mixture; and a two-hour 1900° F. argon heating cycle. The thickness of the titanium was calculated from the weight gained during titanizing. Samples were chosen containing 0.001, 0.003 and 0.005 inch equivalent thickness of titanium. The nominal average composition was calculated from weight gain and metallographic measurements to be approximately 60-70 a/o Ti.

Coated samples of each group were oxidized at 1100° F., 1800° F., 2000° F. and 2300° F. and compared with the performance of untitanized aluminized samples. The samples were removed for weighing after 1, 3, 8, 24, 48, 72, etc., hours until failure was indicated by an abrupt change in the slope of the curve coupled with some visual evidence of local oxidation of the base material. In each case the base material was a columbium alloy of the composition Cb-5 w/o Mo-2 w/o Ti-2 w/o Zr. The tests were cyclic oxidation tests since the samples received exposure to room temperature approximately 20 times in 500 hours.

The oxidation performance of the samples is charted in FIGS. 1 and 2. FIG. 1 graphs the weight gain of the samples against oxidation time at 2300° F., whereas FIG. 2 charts the oxidation life of the samples at temperatures ranging from 1100° F. to 2300° F. These curves show that the coating with the 1 mil titanized zone has the most nearly idealized characteristics as the oxidation life is relatively constant over a wide temperature range. The coatings with thicker (3 mil and 5 mil) titanized zones are more reliable for lower temperature applications but are less reliable at higher temperatures.

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EXAMPLE

The following specific example illustrates the oxidation life of a columbium alloy coated in accordance with this invention: In each instance the alloy was titanized for 17 hours at 1880° F. in a vacuum, after which it was calorized for 4 hours at 1900° F. in argon in 40% (Al-10% Cr)-2% NH₄Cl-58% Al₂O₃:

Base Alloy	Test Temperature, F.	Oxidation Life, hours
Cb-5 w/o Mo-2 w/o Ti-2 w/o Zr-----	1,100	700
	1,800	570
	2,000	547
	2,300	56-80

Having described the invention, we claim:

1. The method of coating columbium and columbium base alloys for protection against oxidation in air at temperatures of from about 1100° F. to 2300° F. that consists in the steps of:

- cleaning the surface of a metal selected from the group consisting of columbium and its alloys,
- titanizing the surface of the metal to establish thereon a titanium rich zone 1 to 5 mils in thickness, and
- pack calorizing the coated metal to deposit thereon a protective aluminum alloy coating.

2. The method of claim 1 wherein the metal alloy consists of Cb-5 w/o Mo-2 w/o Ti-2 w/o Zr.

3. The method of claim 1 wherein the metal alloy is Cb-1 w/o Zr.

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4. The method of claim 1 wherein the alloy is Cb-6.25 w/o Ti.

5. The method of claim 2 wherein the titanizing step consists in heating the metal in the presence of titanium sponge and a volatile halide in a vacuum for a period of about 16 to 17 hours at a temperature of about 1850° to 2400° F.

6. The method of claim 5 wherein the pack calorizing mix consists of 10-60 w/o metal powder (selected from the group consisting of aluminum, Al-11 w/o Si, Al-5 w/o Cr, Al-10 w/o Cr and Al-10 Si-10 Cr)-2 w/o ammonium chloride and the balance aluminum oxide, and the calorizing is performed in argon at a temperature of about 1300° F.-1900° F. for a period of 1 to 4 hours.

7. The method of protectively coating Cb-5 w/o Mo-2 w/o Ti-2 W/o Zr against oxidation in air at temperatures of 1100° F. to 2300° F. that consists in the steps of:

- grit blasting the columbium alloy to clean the surface thereof,
- titanizing the columbium alloy at a temperature of about 1880° F. for 17 hours in a vacuum, and
- pack calorizing the titanized article in argon at a temperature of about 1900° F. for a period of about 4 hours using a calorizing powder consisting of 40 w/o of a metal powder consisting of Al-10 w/o Cr-2 w/o NH₄Cl-58 w/o Al₂O₃.

No references cited.

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