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CORROSION RESISTANT BERYLLIUM BODIES

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1 Claim

This application is a continuation of application Ser. No. 670,486, filed Aug. 11, 1967, which is a division of our pending application Ser. No. 395,012, filed Sept. 8, 1964 and titled "Corrosion Resistant Beryllium Bodies and Method for Producing Same," and which is directed to the method and bath, the present application being directed to the beryllium body.

This invention relates generally to beryllium bodies having a corrosion resistant surface coating, and to a method for application of such a coating.

More specifically, the invention relates to anodized beryllium bodies having a corrosion resistant surface coating, and to a method for anodizing the surface of said bodies.

Beryllium metal has become well established for applications in inertial guidance systems, structural components for aircraft and aerospace use, and in other fields where its properties of lightness, high strength at elevated temperatures and its high strength to weight ratio are desirable characteristics.

However, commercially available beryllium is subject to corrosion by various environments, including high temperature air, tap water, deionized water, and salt spray. Various attempts have been made to provide corrosion resistant beryllium materials. Ceramic coatings have been applied to beryllium surfaces, and various methods of anodizing beryllium surfaces have been used, but all such previously developed methods have failed to provide the desirable combination of properties obtained by the present method.

The present method provides corrosion resistant beryllium materials which greatly extend the application of beryllium in various fields, and was developed as a result of extensive investigation.

A primary object of the invention is to provide anodized corrosion resistant beryllium bodies.

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A further object is to provide beryllium bodies resistant to corrosion in high temperature air, water, deionized water, and salt spray environments.

A still further object of the invention is to provide a method for applying a corrosion resistant coating to the beryllium surface of bodies.

Another object of the invention is to provide a method for anodizing the beryllium surfaces of bodies to render them corrosion resistant to high temperature, water, deionized water, and salt spray environments.

Other objects and advantages of the invention will become apparent from the following description.

The method comprises applying a protective surface coating to beryllium surfaces of bodies by passing an electric current to the beryllium surface connected as an anode, in a bath consisting essentially of water, sodium chromate in an amount of at least 0.4%, by weight, of the bath, and an amount of chormic acid sufficient to adjust the pH range of the bath from about 5.5 to about 7.5, preferably to about 7.0.

The concentration of the sodium chromate solution ranges generally from about 0.4% to about 10%, by weight of the bath, and preferably is used at a 5% weight concentration. The use of sodium chromate in excess of 10% does not appear to increase the effectiveness of the method or coating appreciably.

The bath should be free of hydrochloric and sulfuric acids, as their presence prevents formation of the desired protective coating.

The temperature of the bath must be maintained below about 130° F., since the coating applied above this temperature does not afford proper protective resistance. The temperature of the bath should be less than 130° F., ranging from about 70° F. to about 110° F., and is preferably about 75° F.

For optimum resistance of the protective coating, the solution of sodium chromate should be prepared with distilled water and the pH adjusted with reagent grade chromic acid. The current density may vary from about 48 to about 300 amperes per square foot, and is preferably maintained at from about 150 to about 200 amperes per square foot.

Examples of beryllium bodies protectively coated by the method of the invention and exposed to high-temperature air environment are presented in the following Table I. In each example, a beryllium coupon 0.50" wide, 1.25" long and 0.1875" thick was protectively coated under the various processing conditions set forth in Table I.

TABLE I.—PROCESS VARIABLES

Example No.	Voltage	Current density, amps/ft. ²	Time (min.)	Wt. conc. of sodium chromate, percent	pH	Temperature of bath in ° F.	Hours tested in 800° C. dry air	Physical condition of specimen after test exposure
Effect of anodizing time								
1.....	12	170	10	5	7.0	75	96	No attack or failure.
2.....	12	177	20	5	7.0	75	96	Do.
3.....	12	166	30	5	7.0	75	96	Do.
4.....	12	173	40	5	7.0	75	96	Do.
5.....	12	162	50	5	7.0	75	96	Do.
6.....	12	166	60	5	7.0	75	96	Do.
Effect of current density								
7.....	10	49	60	5	7.0	75	96	No attack or failure.
8.....	9	99	60	5	7.0	75	96	Do.
9.....	12	150	60	5	7.0	75	96	Do.
10.....	12	199	60	5	7.0	75	96	Do.
11.....	12	298	60	5	7.0	75	96	Do.
Effect of solution concentration								
12.....	12	166	90	1	7.0	75	161	No attack or failure.
13.....	12	160	60	2	7.0	75	161	Do.
14.....	12	162	60	5	7.0	75	161	Do.
15.....	9	160	60	10	7.0	75	161	Do.

TABLE I—Continued

Example No.	Voltage	Current density, amps/ft. ²	Time (min.)	Wt. conc. of sodium chromate, percent	pH	Temperature of bath in ° F.	Hours tested in 800° C. dry air	Physical condition of specimen after test exposure
Effect of increased voltage								
16.....	18	162	10	1.5	7.0	75	282	No attack or failure.
17.....	24	96	10	0.6	7.0	75	282	Do.
18.....	24	166	10	1	7.0	75	137	Do.
19.....	60	160	30	0.4	7.0	75	96	Do.
Effect of temperature variation								
							Hours tested in 1,489° F.—1,659° F. dry air	
20.....	12	160	20	5	7.0	111	203	No attack or failure.
21.....	12	160	60	5	7.0	176	65	Failed, corroded.
22.....	12	160	60	5	7.0	140	65	Do.
23.....	12	160	60	5	7.0	75	203	No attack or failure.
24.....	12	160	60	5	7.0	129	174	Do.

Table II shows the effect of exposure to various testing environments of bodies protectively coated at the process conditions specified in the table.

face of the base metal, the overall dimensional change is less than 0.0001" per side, during application time of up to 60 minutes. The small dimensional change in the

TABLE II.—EXPOSURE TESTS OF ANODIZED BERYLLIUM BODIES

Example No.	Beryllium body size	Test environment	Duration of test, hrs.	Condition of bodies
1.....	1" high x 1/2" diameter.....	800° C. in 1% moist air.....	1,749	No attack or failure of anodic coating.
2.....	1 1/4 x 1/2 x 3/16".....	850° C. in dry, CO ₂ free air.....	185	Do.
3.....	1 1/4 x 1/2 x 3/16".....	900° C. in dry CO ₂ free air.....	137	Do.
4.....	1 1/4 x 1/2 x 3/16".....	1,000° C. in dry CO ₂ free air.....	137	Do.
5.....	1 1/4 x 1/2 x 3/16".....	1,100° C. in dry CO ₂ free air.....	113	Do.
6.....	1/2 x 3/8 x 1/8".....	700° C. in dry O ₂	100	No attack or failure of anodic coating, wt. gain ≈ 0.1 mg./cm. ²
7.....	1/2 x 3/8 x 1/8".....	817° C. in dry O ₂	60	No attack or failure of anodic coating, wt. gain = 0.33 mg./cm. ²
8.....	1/2 x 1/4 x 1/8".....	1,030° C. in dry O ₂		No attack or failure of anodic coating, wt. gain = 0.58 mg./cm. ²
9.....	1/8" thick x 2 3/16" diameter.....	5% NaCl salt spray.....	120	No attack or failure of anodic coating.
10.....	3" x 1" x 1/8".....	20% NaCl salt spray.....	24	Do.
11.....	3" x 1" x 1/8".....	110° F. deionized water.....	1,656	Do.
12.....	1" x 1/4" x 1/8".....	Tap water.....	2,160	Do.
13.....	1" x 1/4" x 1/8".....	0.1 N NaCl solan.....	336	Do.

¹ All specimens included in Table II were anodized in a bath containing 5 weight percent sodium chromate with the pH adjusted to 7.0 with chromic acid at a temperature of 75° F., 12 volts and a current density of 160 amperes/ft.²

It will be noted from Tables I and II that all the bodies with the exception of those protectively coated in Examples 21 and 22 of Table I at a bath temperature above 130° F., were completely protected from oxidation. No failure of the protective coating other than a slight change in color occurred, during test exposure of body specimens of all the other examples. Commercial beryllium when exposed to the same conditions normally oxidizes after 48 hours exposure to the extent that 25 to 50% of the test pieces will have been reduced to a fluffy powdered oxidation product.

A comparison exposure test of commercial beryllium specimens with the anodized bodies of Examples 6–8 inclusive, of Table II, showed that after exposure in one atmosphere of dry oxygen at 705° C. for 75 hours, 807° C. for 45 hours, and 1030° C. for 35 hours, the commercial specimens incurred a weight gain of 17.0, 63.0, and 37.0 mg./cm.², respectively, a pronounced increase in weight compared to the weight gained by bodies of the examples even though the commercial specimens were tested for a shorter time at approximately the same temperatures. The examples thus illustrate the high corrosion resistance of the beryllium bodies, the surfaces of which are coated in accordance with the method of the invention.

The examples are presented as illustrative embodiments of the invention and include the preferred embodiments known at the time of preparation of the specification.

Although the method of applying the protective coating to beryllium bodies results in some dissolution of the sur-

face is the result of replacement of the removed beryllium by a protective coating, the volume of which is approximately equivalent to that of the removed metal.

Thus, the negligible dimensional change which occurs in the surface during application of the protective coating is unexpected, as beryllium oxide is known to occupy a larger volume than the amount of beryllium metal stoichiometrically required to produce a given quantity of oxide. The final surface of the protectively coated body is identical in surface pattern with the original body surface, as the degree of polish, machining marks, and blemishes are faithfully reproduced.

The coatings applied by the method of the invention are quite dense and relatively thick. Generally, the thickness of the coating varies from 0.1–2.4 mils, but preferably is about 0.5 mils, dependent upon the control of the process conditions.

The protective coating applied is believed to be a form of hydrated beryllium oxide as it is nearly amorphous in the initially deposited form, as indicated by X-ray analysis. When heated at elevated temperature for a sufficient time, the initial coating is converted to normal crystalline beryllium oxide, as evidenced by X-ray diffraction analysis. Temperatures of about 800° C. may be employed for effecting conversion to the crystalline state.

Having thus described our invention, we claim:

1. A beryllium body having an electrolytically deposited crystalline beryllium oxide coating adherent to the body surface produced by immersing the uncoated body in a

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bath consisting essentially of water, sodium chromate in an amount at least 0.4%, by weight, of the bath, and an amount of chromic acid sufficient to adjust the pH of the bath into a range from about 5.5 to about 7.5, the temperature of the said bath being below about 130° F., and passing an electric current to the surface with the surface connected as an anode.

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