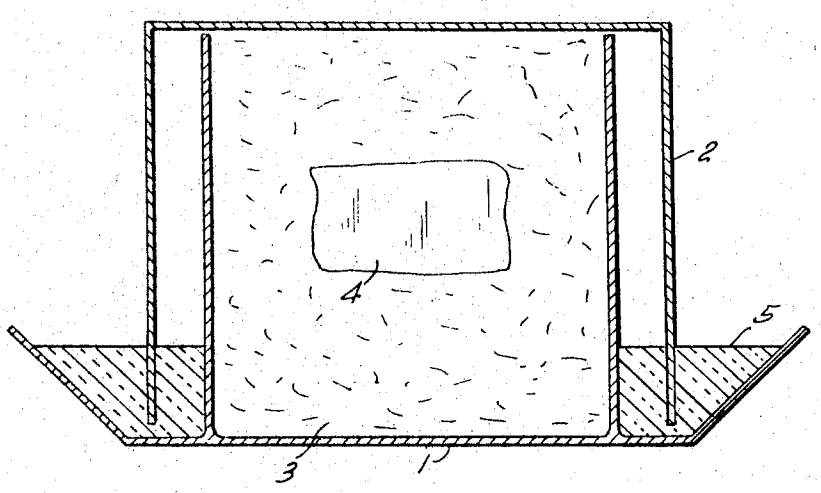
Aug. 26, 1969 D. H. MAXWELL ET AL 3,462,820

COATED COBALT ALLOYS

Original Filed Oct. 21, 1964



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United States Patent Office

3,462,820

Patented Aug. 26, 1969

3,462,820

COATED COBALT ALLOYS

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Original application Oct. 21, 1964, Ser. No. 405,532, now Patent No. 3,343,982, dated Sept. 26, 1967. Divided and this application Aug. 9, 1967, Ser. No. 678,123

Int. Cl. B23p 3/00; C23c 9/00

U.S. Cl. 29—197 3 Claims

ABSTRACT OF THE DISCLOSURE

The invention provides an article resistant to oxidation at elevated temperatures, such as a gas turbine rotor vane or stator blade formed of a cobalt alloy base containing 35% or more cobalt which is enclosed within an outer diffusion coating comprising chromium, aluminum and magnesium up to 5% by weight of the aluminum, the coating being produced from a powder pack in which the magnesium was present in an amount up to 15% by weight of the aluminum.

Cross-reference

This application is a division of our prior application Ser. No. 405,532 filed Oct. 21, 1964.

This invention relates to the treatment of high cobalt alloys to render them resistant to erosion due to oxidation at elevated temperatures.

Gas turbine blades such as rotor blades and stator vanes require the use of metal alloys which are dimensionally stable for long periods of time at elevated temperatures. Many cobalt alloys have been found to possess satisfactory dimensional stability at normal operating temperatures. However, at temperatures as high as 2100° F., many of the conventional cobalt alloys show a tendency toward excessive oxidation and erosion of the oxidation product.

It has been proposed heretofore to coat various high temperature alloys with chromium or aluminum in order to increase their oxidation resistance. However, cobalt alloys coated by conventional means still show a significant decrease in weight i.e., erosion due to oxidation, when held at 2100° F., for 50 to 100 hours. It has now been found that superior oxidation resistance can be achieved if high cobalt alloys are diffusion coated with a mixture of chromium and an aluminum-magnesium alloy containing about 15% magnesium. The thickness of the diffusion coating is not very great, being on the order of from about 0.001" to 0.005". Such coated high cobalt alloys are resistant to erosion due to oxidation for period of 100 hours or more at 2100° F.

The pack diffusion method of applying the diffusion coating is employed in this invention. Generally, in the process of this invention, the shaped alloy to be coated is embedded in a retort or other suitable container containing a predetermined mixture of granular chromium metal, granular aluminum-magnesium alloy, a chromium halide, preferably chromic chloride, and an iodine source such as elemental iodine or ammonium iodide. The retort or other container is treated to remove air, sealed and sintered in a hydrogen or other inert gas atmosphere for the time and temperature, generally above 1800° F., sufficient to obtain the desired coating thickness and degree of diffusion.

Cobalt alloys to be treated in accordance with this invention generally contain at least about 35% of cobalt. Preferably the alloy contains at least about 50% cobalt and about 15% to 27% by weight of chromium. Excellent

results are obtained when such cobalt-chromium alloys also contain from 0% to 12% of nickel, from 5% to 12% of tungsten, from 0% to 1% of titanium, from 0.4% to 1.2% of carbon, and from 0.05% to 2.5% of zirconium. In some instances, the presence of other trace materials is desirable including up to 10% tantalum, up to 3% columbium, up to 0.01% boron, up to 1.5% iron, up to 0.2% manganese, and up to 0.2% silicon. Traces of such impurities as sulfur, phosphorus and copper and the like in amounts which do not detract from the thermal resistance of the basic cobalt alloy can also be present.

A preferred alloy for treatment in accordance with this invention is a commercial alloy known as SM–302 which has the following nominal chemical analysis:

	Percent by weight
Chromium	21.5
Tungsten	10.0
Tantalum	9.0
Zirconium	0.25
Iron	1.0
Nickel	max. 1.5
Boron	0.01
Carbon	0.86
Cobalt	Remainder

Alloy WI–52 is a cobalt base alloy having relatively large amounts of chromium and tungsten in its composition which is specified as follows:

	Percent by weight
Carbon	0.40–0.50
Manganese	max. 0.50
Phosphorus	max. 0.040
Sulfur	max. 0.040
Silicon	max. 0.50
Chromium	20.00–22.00
Tungsten	10.00–12.00
Columbium+tantalum	1.50–2.50
Iron	1.00–2.50
Nickel	max. 1.00
Cobalt	Remainder

Alloy X–40 is a cobalt base alloy having the following specification analysis:

Carbon	0.45–0.55
Manganese	max. 1.0
Silicon	max. 1.0
Phosphorus	max. 0.04
Sulfur	max. 0.04
Chromium	24.5–26.5
Nickel	9.5–11.5
Tungsten	7.0–8.0
Iron	max. 2.0
Cobalt	Remainder

The granular composition making up the pack would generally contain from about 0.5% to 2% by weight of chromium metal, from 1.5% to 3% by weight of the aluminum magnesium alloy containing from 10% to 20% magnesium, from 0.005 to 0.008 by weight of a chromic halide, preferably chromic chloride and from 0.001% to .005% by weight of either elemental iodine or ammonium iodide and from 95% to 98% by weight of an inert carrier material. The preferred inert carrier material is activated alumina, i.e., aluminum oxide, although other materials such as baked kaolin and magnesium oxide can also be employed.

The preferred composition contains about 1% by weight of chromium, about 2% by weight of an aluminum-magnesium alloy, containing 15% by weight of magnesium, about 0.005% by weight of chromic chloride, about 0.001% by weight of either elemental iodine or

ammonium iodide and about 97% by weight of activated aluminum oxide.

The granular material should be finely divided and will be sufficiently fine to pass through a 50 mesh sieve and preferably through a 75 mesh sieve.

FIGURE 1 represents a suitable container for use in carrying out the method of this invention. This container consists of an inner retort **1** having a cover **2** both fabricated of any substance capable of withstanding the temperatures of operation. Deposited within the container is the granulated packing material **3** having been the composition described above and embedded within the packing material are one or more shaped cobalt alloy particles **4** to be coated. A glass ring **5** surrounds the inner retort at its contact point with cover **2**.

In operation, the alloy to be coated is first cleaned by sand blasting and is then subsequently heat treated in a hydrogen atmosphere to remove any traces of an oxide layer. The treated alloy is then embedded in the powder mixture within container **1**. The container is closed and placed in a suitable heating device such as a muffle furnace equipped with a gas-tight door and containing gas inlet and outlet ports. The heating device is purged with an inert gas such as helium or argon to remove the air, and thereupon the protective gas to be employed in the process, either hydrogen or an inert gas such as helium or argon is supplied. Hydrogen is preferred. The temperature within the heating device is raised to a temperature of from 300° F. to 500° F., preferably about 400° F. and maintained for a short time to remove any moisture contained within the system. The temperature is then raised slowly to just below the melting point of the glass **5** to allow the system to come to equilibrium temperature and to allow any remaining air or other gases to leave the retort. The temperature is then raised to above the melting point of the glass ring **5**, thereby causing the glass to melt and form a liquid seal isolating completely the contents of the container from the outside environment. Thereupon the heating device is allowed to come to the diffusion temperature, about 1800° F. to 2200° F. and maintained there for the desired time, generally from 8 to 16 hours. The particular time and temperature employed will, of course, vary within the suggested range depending upon the exact composition of the alloy and the desired amount of coating to be applied.

The following example represents the preferred mode of carrying out the invention.

Two samples of SM–302 alloy, a high cobalt alloy described above, were sand blasted and heated in a hydrogen atmosphere at a temperature of 2000–2100° F. for two to four hours to remove any surface oxide coating. The alloy articles were then embedded in 2000 grams of a granular powder mixture within a retort. This granular powder contained 97% by weight of 100 mesh activated alumina, 2% by weight of a 100–250 mesh aluminum-magnesium alloy containing 85% aluminum and 15% magnesium, 1% of a 100 mesh chromium metal, 0.005% of chromic chloride and 0.001% of elemental iodine. This powder and treatment produces a coating in which the magnesium component is present in an amount up to 5% by weight of the aluminum component.

The retort employed was that illustrated in FIGURE 1. After the retort was closed with the top and the glass ring, it was placed in an oven equipped with gas inlet and outlet ports and purged with argon to remove the air and thereupon hydrogen gas was admitted and the furnace was held at a temperature of 400° F. for 30 minutes to remove any moisture contained in the mixture. The temperature of the furnace was then raised at the rate of 200° F. per hour to about 1200° F., to allow the system to come to equilibrium temperature and to allow any remaining air to escape from the retort. Thereupon the temperature was raised to 1350° F., 50° above the melting point of the glass and maintained for 30 minutes while the glass melted and formed a liquid seal. Thereupon the temperature was raised to 2050° F. and maintained for 16 hours. At the conclusion of this period, the furnace was allowed to cool, the glass seal was broken and the diffusion coated alloy removed. Upon testing, none of the samples showed any weight loss after being heated for 100 hours at 2100° F., indicating that the coating method of this invention is well suited for use in protecting gas turbine blades from erosion due to oxidation. One of the samples showed a negligible weight increase at the end of 100 hours of about 0.4%, while the other sample showed an equally negligible weight increase of about 1.6%. This contrasts with an uncoated alloy which would show a weight loss of 12% or more when heated for even as much as 60 or 70 hours at 2100° F.

Similar results are obtained when other high cobalt alloys are employed.

We claim:

1. A metal article resistant to oxidation at elevated temperatures comprising a homogeneous cobalt alloy base, containing at least about 35% cobalt, enclosed within an outer diffusion coating comprising chromium, aluminum and magnesium, the magnesium component being present in an amount up to 5% by weight of the aluminum component.

2. A metal article as in claim **1** in the form of a gas turbine rotor blade.

3. A metal article as inc laim **1** in the form of a gas turbine stator vane.

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HYLAND BIZOT, Primary Examiner

U.S. Cl. X.R.

29—183, 194, 198