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[54] METHOD FOR SURFACE TREATMENT OF NICKEL AND COBALT BASE ALLOYS

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[58] **Field of Search** .....204/38 S; 117/107.2 P; 148/187–188

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[57] **ABSTRACT**

The treatment of high nickel and cobalt base alloy to improve the corrosion resistance of parts formed thereof by first applying a coating of nickel and then subjecting the part to diffusion coating to aluminize the surface.

14 Claims, No Drawings

METHOD FOR SURFACE TREATMENT OF NICKEL AND COBALT BASE ALLOYS

This invention relates to the art of aluminizing metal surfaces by diffusion to provide a surface on the metal which is rendered more resistant to corrosion or oxidation at high temperatures and/or in corrosive atmospheres, such as exist in a combustion engine, turbine, and the like. By diffusion of aluminum into the surface of such metals as high nickel or cobalt alloys and high alloy steels, heat shock erosion, corrosion resistance and other physical and mechanical properties are markedly improved.

To the present, in the aluminizing treatment by diffusion coating, the metal part is heated to a temperature above 1000° C. in a pack formed of a powdered mixture of metallic aluminum and aluminum oxides, without and preferably with a small amount of halide salt such as ammonium chloride or ammonium fluoride, for about 4 to 10 hours in a nonoxidizing atmosphere.

The aluminum diffuses into the surface, usually to a depth within the range of about 10–20 microns, depending somewhat upon the time and temperature of the aluminizing treatment and the amount of aluminum in the pack, with the amount of aluminum in the diffusion layer decreasing from the surface inwardly toward the center in amounts somewhat proportionate to the distance from the surface.

It is an object of this invention to provide an improved aluminized article and method for preparation of same wherein the diffusion coating of aluminum remains concentrated in a narrow layer on the surface of the article without excessive diffusion into the interior of the article; whereby a better bond is achieved between the diffusion coating and metal substrate; and whereby a complex series of compounds are formed in the diffusion layer to provide an improved coating which offers higher temperature corrosion resistance.

In accordance with the practice of this invention, the parts formed of a superalloy, and preferably nickel and cobalt based alloys, are first processed to provide the surface portions to be aluminized with a thin coating of nickel, in a first coating step. The coated parts are then packed in the conventional manner and conventional compositions for aluminizing the surface by diffusion transfer of aluminum. The presence of nickel as a precoat on the metal surface is believed to operate as a barrier coat which concentrates the diffused aluminum in the surface portions of the metal parts to provide an aluminized surface having greatly improved corrosion resistance, especially when measured at high temperature and in the presence of highly corrosive gases.

In the described two-stage process of first nickel plating and then diffusion coating to aluminize the plated surface by a pack cementation process it is desirable to deposit a nickel coating in the first stage having a thickness greater than 0.0001 inch and preferably having a thickness within the range of 0.0001 to 0.001 inch.

The desired thickness of nickel coating can be deposited by conventional electroplating processes, such as described in the article published by the ASM Committee on Nickel Plating, entitled Nickel Plating, published in the *Metals Handbook*, Volume II, pages 432–443, under general purpose plating baths. Instead, the desired thickness of nickel coating can be deposited on the surface of the parts nonelectrically, as described on pages 443–445 of the *Metals Handbook*, Volume II, supra, under the heading Nonelectrolytic Nickel Plating.

The aluminizing pack employed in the pack cementation process for aluminizing the nickel-coated surfaces can be formulated to contain aluminum metal in finely divided form in an amount within the range of 0.1 to 10 percent by weight with the remainder formed of a finely divided filler, preferably alumina. Although it is not essential, use can be made of an energizer, such as ammonium chloride or ammonium fluoride, in an amount within the range of 0.01 to 5 percent by weight of the pack. A hydrogen or inert atmosphere is maintained during diffusion coating while the materials are heated to a temperature within the range of 1,800° to 1,200° F. or a time sufficient to build up a final coating thickness within the range of 0.001 to 0.005 and preferably within the range of 0.0015 to 0.003 inch. The desired coating thickness is obtained with a pack of the type described in about 9 to 10 hours of heating.

The following examples are given by way of illustration, but not by way of limitation, of the practice of this invention:

Alloy Composition:

Example 1

	Percent by Weight
Ni	70.0
Cr	12.0
W	5.0
Al	5.0
Mo	3.5
Ti, Nb, Ta	2.5
Fe, C, Mn, Si	Balance

Example 2

	Percent by Weight
Co	60.0
Cr	20.0
W	10.0
Nb	2.0
Ni	1.0
Fe, C, Mn, Si	Balance

Example 3

	Percent by Weight
C	0.08
Mn	0.75
Si	0.75
Cr	19.0
Co	19.5
Mo	4.0
Ti	2.9
Al	2.9
Fe	4.0
Ni	Balance

Example 4

	Percent by Weight
C	0.12
Mn	0.15
Si	0.4
Cr	13.0
Mo	4.5
Ti	0.6
Al	6.0
Fe	1.0
Cb	2.25
Ni	Balance

First stage of nickel coating:

Example 5

Composition of Electrolytic Bath

Nickel sulfate, $NiSO_4 6H_2O$	30 to 55
Nickel chloride, $NiCl_2 6H_2O$	4 to 8(a)
Nickel sulfamate, $Ni(SO_3NH_2)_2$	—
Nickel fluoborate, $Ni(BF_4)_2$	—
Total nickel as metal	7.7 to 14.2
Boric acid, H_3BO_3	4 to 6
Antipitting additives	(b)

Operating Conditions

pH	1.5 to 5.2
Temperature F.	115 to 160
Current density, a. per sq. ft.	10 to 100

Example 6

Composition of Electrolytic Bath

Nickel sulfate, $NiSO_4 6H_2O$	—
Nickel chloride, $NiCl_2 6H_2O$	0 to 4
Nickel sulfamate, $Ni(SO_3NH_2)_2$	35 to 60
Nickel fluoborate, $Ni(BF_4)_2$	—
Total nickel as metal	8.2 to 15
Boric acid, H_3BO_3	4 to 6
Antipitting additives	(b)

Operating Conditions

pH	3 to 5
Temperature F.	100 to 140
Current density, a. per sq. ft.	25 to 300

Example 7

Composition of Electrolytic Bath

Nickel sulfate, $NiSO_4 6H_2O$	—
Nickel chloride, $NiCl_2 6H_2O$	0 to 2
Nickel sulfamate, $Ni(SO_3NH_2)_2$	—
Nickel fluoborate, $Ni(BF_4)_2$	30 to 40
Total nickel as metal	7.6 to 10.5
Boric acid, H_3BO_3	2 to 4
Antipitting additives	(b)

Operating Conditions

pH	2.5 to 4
Temperature, F.	100 to 160
Current density, a. per sq. ft.	25 to 300

Example 8

Composition Nonelectrolytic Bath

Nickel chloride ($NiCl_2 6H_2O$	80 oz. per gal.
Boric acid (H_3BO_3)	4 oz. per gal.

Operating Conditions

pH	3.5 to 4.5
Temperature	160° F.

Example 9

Composition Nonelectrolytic Bath

Nickel chloride	30
Nickel sulfate	—
Sodium hypophosphite	10
Sodium acetate	—
Sodium hydroxyacetate	50
Sodium succinate	—
Lactic acid (80%)	—
Propionic acid (100%)	—

Operating Conditions

pH	4 to 6
Temperature, F.	190 to 210
Plating rate (approx.), mil per hr.	0.5

Example 10

Aluminizing Pack:	
5 pounds	powdered aluminum metal
100 pounds	powdered alumina

Example 11

7 pounds	powdered aluminum metal
100 pounds	powdered alumina
0.2 pound	ammonium chloride

In the electrolytic plating systems of Examples 5 to 7, the part is suspended as a cathode in the electrolyte until a coating thickness within the range of 0.0001 to 0.001 inch has been deposited. The part is then removed and rinsed with water to remove electrolytic.

In the nonelectrolytic systems of Examples 8 and 9, a thinner nickel coating is deposited on the metal surfaces. In practice, the parts are immersed in the bath with continuous movement until a nickel coating having a thickness within the range of 0.0001 to 0.001 inch is deposited and the part is then removed and rinsed.

The nickel plated parts are packed with the pack composition of Examples 10 and 11 in a retort. The parts formed of the cobalt alloy of Example 2 are heated in a hydrogen atmosphere for 10 hours at 1950° F. while the parts formed of the nickel-based alloys of Examples 1, 3 and 4 are heated in a hydrogen atmosphere for 9 hours at 1,950° F. to form parts having a final coating thickness within the range of 0.0015 to 0.003 inch.

Instead of making use of the nickel or cobalt based alloys of Examples 1 to 4, use can be made of parts formed of nickel or cobalt based superalloys in which corrosion resistance at high temperature and resistance to deterioration by the sulfides present in corrosive gases is greatly improved.

The term "powdered" or "finely divided" form, as applied to the elements in the pack composition, is meant to refer to aluminum metal particles of preferably less than 5 microns and is meant to refer to particles of less than 100 microns and preferably within the range of 5–100 microns for the filler or alumina component of each pack.

It will be understood that changes may be made in the details of formulation and operation without departing from the spirit of the invention, especially as defined in the following claims.

We claim:

1. A method for surface treatment to improve the corrosion resistance of products having surface portions formed of a metal selected from the group consisting of nickel base alloys, cobalt base alloys, and superalloys, comprising the steps of applying a first coating of nickel on surfaces of the product, and then aluminizing the nickel coated surfaces by diffusion transfer.

2. The method as claimed in claim 1 in which the first coating of nickel is applied in a coating thickness greater than 0.0001 inch.

3. The method as claimed in claim 1 in which the first coating of nickel is applied by a nonelectrolytic system in a coating thickness within the range of 0.0001 to 0.001 inch.

4. The method as claimed in claim 1 in which the first coating of nickel is applied in a coating thickness within the range of 0.0001 to 0.001 inch.

5. The method as claimed in claim 1 in which the nickel coating is applied by electroplating the product.

6. The method as claimed in claim 1 in which the nickel coating is deposited by chemical deposition.

7. The method as claimed in claim 1 in which the aluminizing coating is applied with the materials at elevated temperature.

8. The method as claimed in claim 7 in which the materials are applied at elevated temperature within the range of 1,800° to 2,000° F.

9. The method as claimed in claim 1 in which the aluminizing coating is applied in a nonoxidizing temperature.

10. The method as claimed in claim 1 in which the aluminizing coating is applied in an amount to provide an overall coating thickness within the range of 0.001 to 0.005 inch.

11. The method as claimed in claim 1 in which the aluminizing coating is applied in an amount to provide an overall coating thickness within the range of 0.0015 to 0.003 inch.

12. The method as claimed in claim 1 in which the product is aluminized by packing the nickel coated product in an aluminizing composition containing aluminum metal in finely divided form in an amount within the range of 0.1 to 10 percent by weight uniformly distributed in a filler.

13. The method as claimed in claim 12 in which the filler is alumina.

14. The method as claimed in claim 12 in which the aluminizing composition contains an energizer.

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