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Bungardt et al.

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[54] PROTECTIVE DIFFUSION LAYER ON NICKEL AND/OR COBALT-BASED ALLOYS

[75] Inventors: **Karl Bungardt; Gunter Lehnert; Helmut W. Meinhardt,** all of Krefeld, Germany

[73] Assignee: **Deutsche Edelstahlwerke Aktiengesellschaft,** Krefeld, Germany

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Related U.S. Application Data

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** **29/194,** 29/197

[51] **Int. Cl.** **B32b 15/00**

[58] **Field of Search** 29/194, 197; 117/130

[56] **References Cited**

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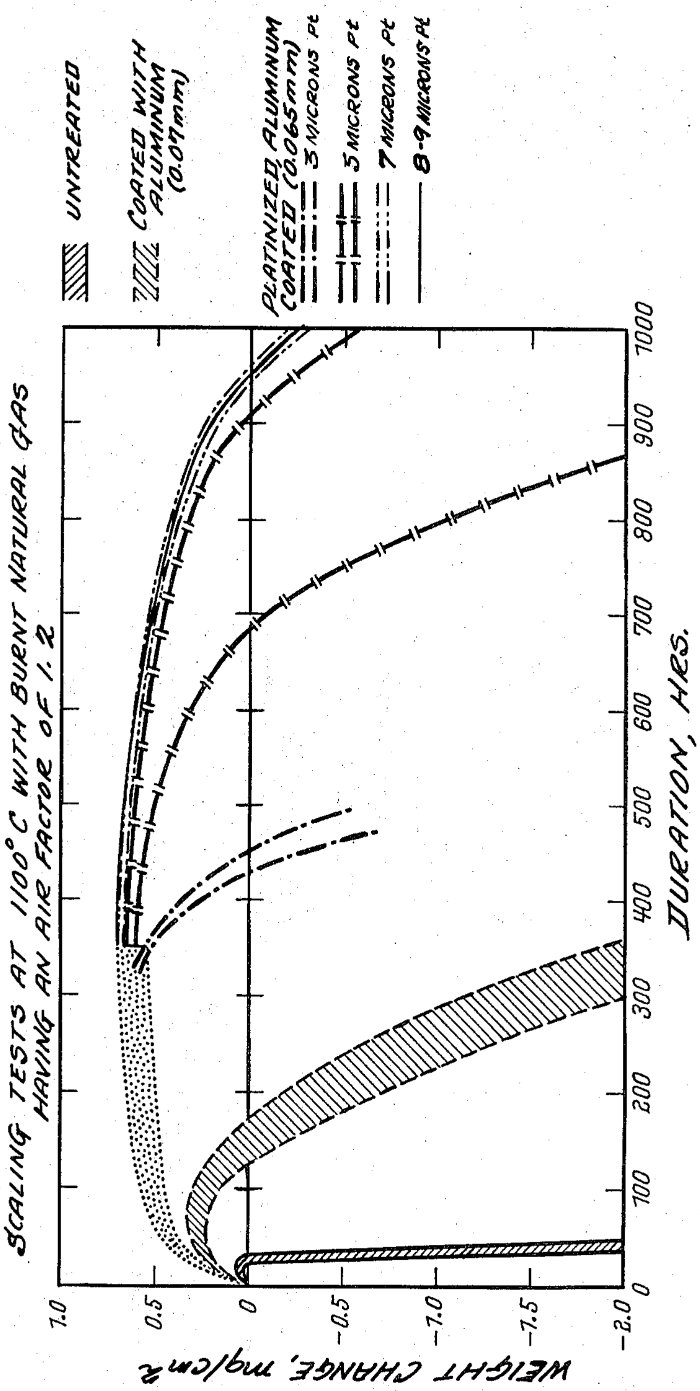
Primary Examiner—L. Dewayne Rutledge
Assistant Examiner—E. L. Weise
Attorney, Agent, or Firm—Cushman, Darby & Cushman

[57] **ABSTRACT**

Nickel and/or cobalt-based alloys are given a protective coating by diffusing into the surface of the alloy metallic aluminum and one or more metals of the platinum groups.

1 Claim, 1 Drawing Figure


SCALING TESTS AT 1100°C WITH BURNT NATURAL GAS
HAVING AN AIR FACTOR OF 1.2
UNTREATED
COATED WITH ALUMINUM (0.07mm)
PLATINIZED ALUMINUM COATED (0.065mm)
3 MICRONS Pt
5 MICRONS Pt
7 MICRONS Pt
8-9 MICRONS Pt
1.0
0.5
0
-0.5
-1.0
-1.5
-2.0
WEIGHT CHANGE, mg/cm²
0
100
200
300
400
500
600
700
800
900
1000
DURATION, HRS.

PROTECTIVE DIFFUSION LAYER ON NICKEL AND/OR COBALT-BASED ALLOYS

This is a division, of application Ser. No. 856,539 filed Sept. 10, 1969 now U.S. Pat. No. 3,677,789 dated July 18, 1972.

This invention relates to the production of high-temperature corrosion and scale-resistant protective diffusion layers on parts made of high-temperature nickel and/or cobalt-based alloys, and to methods of producing such layers.

Parts exposed to the action of corrosive media at high temperatures as well as to mechanical stress, for example turbine blades, are conventionally made of high temperature alloys based on nickel and/or cobalt, and are provided with a protective layer produced by diffusion to render them resistant to corrosion and scaling and thereby to prolong their useful life. For the formation of the protective layer aluminum is preferentially diffused into the surface of such parts. Although parts that have been thus aluminized are particularly resistant to corrosion and scaling, their life, particularly turbine blades, is not as long as would be desirable.

It is therefore the object of the invention to provide parts made of high-temperature alloys that are based on nickel and/or cobalt and that are to be subjected to high mechanical stress and to attack by corrosive media, with a surface layer that will prolong the life of such parts which, primarily due to scaling, will otherwise have a restricted life.

For achieving this object, the present invention provides a protective layer by diffusing into the surface of the parts that are to be protected aluminum and one or more metals of the platinum group of elements, particularly platinum, rhodium and palladium. Tests have shown that parts provided with a protective layer according to the invention have a longer life in service compared with parts into which aluminum alone has been diffused in conventional manner.

One or more metals of the platinum group can be diffused into the parts at the same time as the aluminum, or alternatively in a preferred method of producing the proposed protective diffusion layer according to the invention, one or more metals of the platinum group may first be applied to the surface of the part that is to be protected in the form of a coating at least 7μ thick, and in a following diffusion heat treatment aluminum may then be diffused into the surface together with the metal or metals of the platinum group already deposited. Thus in the said preferred method, the surface of the part that is to be protected is first coated with a metal or metals of the platinum group, and this metal or these metals of the platinum group are then diffused into the surface simultaneously with the aluminum. The said coating of one or more metals of the platinum group may be provided either electrolytically, or by dipping, spraying, vapor deposition or by mechanical plating. During the following diffusion treatment the metal forming this coating together with the aluminum then diffuses into the surface of the part that is to be protected and forms a high-temperature scale-resistant protective layer on the part.

It is also possible to produce a diffused layer according to the invention by first applying to the surface of the part that is to be protected a coating of one or more metals of the platinum group and then applying a further layer of aluminum covering the first coating before the part is submitted to the diffusion treatment, whereby both the metal or metals of the platinum group and the aluminum diffuse into the said surface.

In a further preferred embodiment of the method of the invention the parts that have been provided with a coating of one or more metals of the platinum group may be embedded for the diffusion treatment in a powder mixture containing metallic aluminum.

In general diffusion may be effected by heating between about 900°C and about 1,200°C for about 2 hours to about 10 hours.

The advantages that can be secured by the invention are illustrated by the diagram of the accompanying drawing, wherein the amount of scale formed in mg/sq.cm. is plotted against the time the part is in operative use at 1,100°C. Test pieces provided with a diffusion layer according to the invention were compared with parts having surfaces that were either left unprotected or that had been protected with a conventional diffused layer of aluminum.

The test pieces consisted of an alloy containing 0.12 percent carbon, less than 0.25 percent silicon, less than 0.25 percent manganese, 13.5 percent chromium, 4.5 percent molybdenum, 6.25 percent aluminum, 2.3 percent niobium/tantalum, less than 1.0 percent cobalt, 0.9 percent titanium, less than 1.5 percent iron, traces of boron and zirconium, the remainder being nickel.

The test pieces that had been provided with the protective diffusion layer were first subjected to a preliminary treatment consisting of wet blasting, degreasing in a cyanide bath **10** seconds cathodically and 30 seconds anodically, followed by rinsing in water and anodic pickling at 40°C first 3 seconds in a 10 percent by volume H_2SO_4 bath followed by rinsing in water and then 30 seconds cathodically and 10 seconds anodically, pickling in a 10 percent by weight solution NaOH bath, followed by rinsing in water.

For the production of the diffusion layer according to the invention the test pieces were then platinum coated in a bath consisting of

13 g/l of hexachloroplatinic acid, H_2PtCl_6,
45 g/l of triammonium phosphate, $(NH_4)_3PO_4$,
240 g/l of di-sodium hydrogen phosphate, Na_2HPO_4.

The temperature of the bath was 65°C, the current density 9.0 amp/dm^2 and the voltage 1.5 volts. Different thicknesses of the platinum coating were provided by altering the treatment times accordingly.

After having been platinum coated, the parts were heat treated first for 2 hours at 260°C and then for 3 hours at 400°C to drive off hydrogen and to reduce the hardness of the platinum coating. Finally the surface was degreased by rinsing in methanol.

The test pieces which had thus been heated according to the invention, together with the control pieces, were then submitted to an aluminum diffusion treatment. The test pieces were packed into a powder mixture consisting of 5 percent aluminum and 95 percent Al_2O_3 and diffusion treated for 2½ hours at 1,100°C under hydrogen as a protective gas.

The accompanying diagram reveals the difference in scale formation between completely untreated parts, parts that had been merely diffusion treated with aluminum and parts that had been provided with the protective layer according to the invention, the considerable superiority of which is apparent. Whereas the untreated parts underwent considerable deterioration due to scaling after 20 to 30 hours at the test temperature of 1,100°C, parts that had been subjected to aluminum diffusion in conventional manner did not begin to scale until much later. However, the scaling resistance of the parts provided with the protective layer according to the invention was several times better than the best of the comparative test pieces. Thus when a 7μ platinum layer had been applied the parts still disclosed no significant scaling after 1,000 hours.

When considering the diagram it is to be noted that the areas surrounded by full lines and by dashed lines are the areas of scatter of the results achieved with untreated parts and with parts that had been exclusively aluminized by diffusion, whereas the other indicated lines for parts provided with the protective layers according to the invention relate to individual tests and do not comprise an area of scatter. However, the tendency of the test pieces that had been provided with the diffusion layer according to the invention to last longer is very clearly apparent.

Turbine blades made of the above-specified base material provided with a 7μ platinum coating by electrodeposition in the above-described manner and then submitted to the above-described aluminum diffusion treatment to form a layer having a total depth of 65μ, were also subjected to thermal shock tests to examine their liability to crack. For this purpose the turbine blades were affixed to a wheel which was rotated. Two burners operated with kerosene generated a peak temperature of 1,050°C on the surface of the turbine

blades. After having passed through the burner zones the turbine blades were quenched to about 150°C by exposing them to a blast of compressed air. The heating time in each case was 60 seconds and the quenching time was also 60 seconds.

Simultaneously with this exposure to thermal stress, the turbine blades were subjected to mechanical stresses by mounting them eccentrically on the rotating wheel and thereby subjecting the trailing edges of the turbine blades to tension.

After 10,000 temperature reversals, the turbine blades provided with the protective diffusion layer according to the invention showed no damage due to cracking or chipping. The appearance of the protective surface layer when inspected by the naked eye was still excellent after 10,000 temperature reversals, whereas after the same number of temperature reversals blades that had been provided with other conventional types of surface protection had scaled surfaces as well as cracks.

What we claim is:

1. An object made of an alloy selected from the group consisting of nickel based alloys, cobalt based alloys and nickel/cobalt based alloy having a protective diffusion layer thereon and into the surface thereof, said diffusion layer consisting of the nickel based, cobalt based, or nickel/cobalt based alloy, aluminum and at least one metal of the group consisting of platinum, palladium and rhodium.

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