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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
WASHINGTON, D.C. 20546

MAR 28 1975

REPLY TO: GP  
ATTN OF: GP

TO: KSI/Scientific & Technical Information Division  
Attn: Miss Winnie M. Morgan

FROM: GP/Office of Assistant General  
Counsel for Patent Matters

SUBJECT: Announcement of NASA-Owned U.S. Patents in STAR

In accordance with the procedures agreed upon by Code GP and Code KSI, the attached NASA-owned U.S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No. : 3,869,779

Government or Corporate Employee : U.S. Government

Supplementary Corporate Source (if applicable) : [Signature]

NASA Patent Case No. : LEu-11,696-2

NOTE - If this patent covers an invention made by a corporate employee of a NASA Contractor, the following is applicable:

YES  NO

Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of column No. 1 of the Specification, following the words "...with respect to an invention of ..."

*Bonnie L. Woerner*  
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Enclosure



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(NASA-Case-LEW-11696-2) DUPLEX ALUMINIZED COATINGS Patent (NASA) 4 P CSCL 11C

# United States Patent [19]

Gedwill et al.

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[11] 3,869,779

[45] Mar. 11, 1975

[54] DUPLEX ALUMINIZED COATINGS	3,620,693	11/1971	Sama .....	29/197 X
[75] Inventors: Michael A. Gedwill, North Olmsted;	3,649,225	3/1972	Simmons.....	29/194
Salvatore J. Grisaffe, Rocky River,	3,676,085	7/1972	Evans et al. ....	29/194
both of Ohio	3,741,791	6/1973	Maxwell et al. ....	29/194 X
	3,754,903	8/1973	Goward et al. ....	29/194 X

[73] Assignee: The United States of America as represented by the Administrator of the National Aeronautics and Space Administration, Washington, D.C.

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[21] Appl. No.: 436,315

### Related U.S. Application Data

[62] Division of Ser. No. 298,156, Oct. 16, 1972.

[52] U.S. Cl. .... 29/194, 29/196.2, 29/196.6, 29/197

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

[58] Field of Search ..... 29/194, 196.2, 197, 196.6

### [56] References Cited

#### UNITED STATES PATENTS

3,542,530 11/1970 Talboom et al. .... 29/196.6 X

### [57] ABSTRACT

The surface of a metallic base system is initially coated with a metallic alloy layer that is ductile and oxidation resistant. An aluminide coating is then applied to the metallic alloy layer. The chemistry of the metallic alloy layer is such that the oxidation resistance of the subsequently aluminized outermost layer is not seriously degraded.

9 Claims, No Drawings

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**DUPLEX ALUMINIZED COATINGS****ORIGIN OF THE INVENTION**

The invention described herein was made by employees of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

**RELATED APPLICATION**

This application is a division of copending application, Ser. No. 298,156 which was filed Oct. 16, 1972.

**BACKGROUND OF THE INVENTION**

This invention is concerned with coating metallic base systems. The invention is particularly directed to oxidation resistant alloy overlay coatings and claddings for superalloys and dispersion-strengthened alloys.

Aluminide conversion coatings are currently used to protect superalloy components in aircraft gas turbine engines from oxidation, hot corrosion, thermal fatigue, and erosion. The majority of such coatings are applied by diffusion controlled aluminum enrichment of the superalloy surface. In such a process the substrate chemistry and the processing temperature exert a major influence on coating chemistry, thickness, and properties. Thus, it is difficult to tailor an aluminide coating to resist a particular engine environment. As engine temperatures increase to improve performance, aluminide conversion coatings alone offer less potential for providing long time oxidation and thermal fatigue resistance.

Nickel and cobalt base superalloys and dispersion-strengthened alloys are used as turbine vanes and blades in aircraft and land-based gas turbine engines. Oxidation, hot corrosion, and thermal fatigue cracking are major factors which limit the useful life of those superalloys by providing a more oxidation and hot corrosion resistant surface in which thermal fatigue cracking is reduced.

The aluminide coatings are in themselves made of a hard, brittle outer-layer and a hard, brittle multiphase sub-layer that can crack under high thermal stresses. Once cracked, the oxidizing and/or hot corrosion environment has direct access to the underlying substrate, and deleterious attacks can occur. Also certain elements in the superalloy substrate enter into these coatings. This generally reduces the environmental resistance of the coatings and makes them less ductile.

**SUMMARY OF THE INVENTION**

According to the present invention the substrate is initially overlaid with a ductile, oxidation resistant metallic alloy layer. This overlay is achieved by foil cladding or other means, such as physical vapor deposition, ion plating, sputtering, plasma spraying, or slurry sintering. Foil cladding requires more preliminary effort and fixturing, but it supplies a well characterized homogeneous material directly on the superalloy. Thus it provides the protection potential and metallurgical interactions for weak, oxidation resistant alloy coatings on strong, less environmentally resistant superalloys and dispersion-strengthened alloys.

The chemistry of the overlay coating is such that the oxidation resistance of the subsequently aluminized outermost layer is not seriously degraded. The aluminide outer layer can be developed by pack cementa-

tion, metallizing, dipping, spraying, physical vapor deposition, ion plating, sputtering, or electrophoresis. Thus, a failsafe system is provided. The aluminide outer layer has a tendency to be less embrittled by substrate elements. It has a lessened tendency to crack because it is supported by a ductile layer, not a brittle, multiphase layer that is conventionally the case. If a crack occurs in the aluminide outer-layer, the ductility of the underlayer restricts its propagation. Widespread oxidation of the underlayer does not occur because the metallic underlayer is oxidation resistant.

**OBJECTS OF THE INVENTION**

It is, therefore, an object of the present invention to provide an improved oxidation resistant coating for superalloys and dispersion-strengthened alloys.

Another object of the invention is to provide an aluminized coating having long time oxidation and thermal fatigue resistance for these materials.

A further object of the invention is to provide an improved aluminized coating for nickel base and cobalt base superalloys, dispersion-strengthened alloys, composites, and directional eutectics.

These and other objects of the invention will be apparent from the specification which follows.

**PREFERRED EMBODIMENT OF THE INVENTION**

According to the present invention a ductile, oxidation resistant metallic alloy is initially applied to the superalloy. An aluminide coating is then applied to the metallic alloy.

In order to illustrate the beneficial technical effects of the invention NiCrAlSi and FeCrAlY foil claddings were applied to typical nickel and cobalt base superalloys of the type used in gas turbine engines. The nominal composition of the first mentioned cladding was 15 to 25% chromium, 3 to 6% aluminum, 0.5 to 1.5% silicon, and the remainder nickel. The preferred composition was 18% chromium, 4% aluminum, 1% silicon, and the remainder nickel.

The other cladding had a nominal composition of 15 to 2% chromium, 3 to 6% aluminum, 0.1 to 1% yttrium, and the remainder iron. The preferred composition was 25% chromium, 4% aluminum, 1% yttrium, and the remainder iron.

These claddings were applied to nickel base superalloys known as IN-100 and W1-52. The nominal composition of the IN-100 alloy was 15% cobalt, 9.5% chromium, 5.3% aluminum, 4.3% titanium, 3.2% molybdenum and the remainder nickel. The nominal composition of the W1-52 was 21% chromium, 11% tungsten, 2.2% iron, 1.9% columbium, 0.9% silicon and the remainder cobalt. The claddings were also applied to WAZ-20 and NX-188 advanced superalloys and to TD-NiCr dispersion-strengthened alloy. The nominal compositions were, for WAZ-20, 20% tungsten, 6.5% aluminum, 1.5% zirconium, 0.2% carbon and the remainder nickel; for NX-188, 18% molybdenum, 8% aluminum, 0.04% carbon and the remainder nickel; and for TD-NiCr, 20% chromium, 2% thorium dioxide, and the remainder nickel. It is further contemplated that the substrate can be nickel and cobalt base composites and directional eutectic alloys.

Claddings having a thickness of 0.127 millimeter of both materials were applied to the substrate specimens by hot isostatic gas pressure bonding at a helium pressure of 15,000 to 20,000 psi for two hours at 1090°C.

Aluminide coatings were then applied to the claddings by pack cementation at 1900° to 2000°F in argon using a powder mixture consisting of 1% sodium or ammonium halide, 1% aluminum, and the remainder aluminum oxide. It is also contemplated that the aluminide coating can be applied by a sintered or fused slurry, electrodeposition, physical vapor deposition, ion plating, sputtering, hot dipping, or pyrolysis. The electrodeposition can be of the aqueous, fused salt, or electrophoresis type. The spraying can be either a flame or plasma type.

The system performance was primarily evaluated on the basis of weight change, visual appearance, and metallographic change. Weight change results of furnace tests on NiCrAlSi clad IN-100 and Wi-52 at 1090°C for 20 hour exposure cycles were obtained. These tests showed that the clad-cladding alloy was oxidation resistant in that it gained weight in forming a protective oxide and then little further weight change occurred. While NiCrAlSi clad on IN-100 showed a slight turnaround primarily due to spalling, it was more protective than on Wi-52. Both bare IN-100 and bare Wi-52 lost weight rapidly. Exposure at 1040°C resulted in more protective behavior for both cladding systems for times up to 400 hours.

Metallographic cross sections of the NiCrAlSi cladding on In-100 showed this system was relatively unaffected by 200 hour cyclic furnace oxidation at 1090°C. NiCrAlSi clad Wi-52 showed considerable surface oxide penetration and internal oxidation in the cladding after only 120 hours of tests.

The FeCrAlY cladding was evaluated in cyclic furnace oxidation on In-100 and Wi-52. The 1090°C weight change behavior of the clad Wi-52 was almost identical to that of the cladding alloy itself. The clad In-100, however, showed more rapid weight gains accompanied by significant spalling. A lower exposure temperature of 1040°C resulted in less oxidation attack for the claddings on both substrates.

Metallographic and weight change data obtained after 1090°C furnace tests on the commercial aluminide coatings were compared with similar data with the most protective claddings on each substrate. These comparisons indicated that both the attack on the microstructure and weight changes of the coating and NiCrAlSi cladding on IN-100 were very similar after 200 hours (20 hour cycles) at 1090°C. Here, both protection systems were approximately the same thickness. The FeCrAlY cladding on Wi-52 was in much better condition than the completely degraded coating, but it was about twice as thick in the as-clad condition. This ease in controlling thickness is a beneficial technical effect of the overlay or cladding process.

The most promising cladding systems based on furnace testing were the NiCrAlSi clad IN-100 and the FeCrAlY clad Wi-52; FeCrAlY clad IN-100 also appeared to have some potential. These systems were subjected to Mach 1 burner rig testing at both 1040° and 1090°C using one hour exposure cycles followed by air blast quenching. Such testing imposed significantly greater thermal stress on the protection system and the surface oxide, especially at the leading edges of the burner rig specimens. The FeCrAlY cladding performed better on both IN-100 and WI-52 than did the NiCrAlSi cladding. The thermal fatigue resistance of these clad systems was markedly superior to that of the aluminide coated systems. In all tests, no cracks were

observed in the claddings within the test times. Only the FeCrAlY clad WI-52 performed better in oxidation erosion than the aluminide coating.

Some NiCrAlSi clad IN-100 burner specimens were aluminized to obtain the benefits of both protective systems. Soft ductile claddings had shown superior resistance to thermal fatigue cracking while harder and more brittle aluminide coatings resisted oxidation better. Aluminizing the NiCrAlSi claddings produced a markedly improved protection system for IN-100. The system withstood at least 800 hours of Mach 1 burner rig testing at 1090°C. Based on the time to show weight change turaround, the aluminized cladding was four to five times as protective as the commercial aluminide coating. Its thermal fatigue resistance was about three times better than the aluminide coating.

The primary cause for improvement in thermal fatigue resistance is believed to be the existence of a rather ductile oxidation resistant layer of aluminum enriched cladding under the external aluminide coating. In conventional aluminide coatings on superalloys, a hard, carbide rich zone is typically found here. Benefits may also be derived from the conversion of the relatively simple NiCrAlSi alloy to the aluminide. This aluminide would be expected to contain little of the strengthening elements found in the IN-100.

Several aluminized NiCrAlSi clad WAZ-20, NX-188, and TD-NiCr specimens were tested in cyclic furnace oxidation at 1150°C to see how effective the coating would be for higher temperature applications. The oxidation life of the clad was well in excess of 500 and 300 hours, respectively, on WAZ-20 and NX-188, and slightly more than 600 hours on TC-NiCr. This is a substantial improvement over aluminide coatings alone on these substrates which generally failed well within 100 hours in the same tests.

Burner rig tests at 1090°C and Mach-1 were conducted on aluminized, electron beam melted and physical vapor deposited NiCrAlSi coatings on IN-100 and NASA-TRW VI-A. The nominal composition on the coatings as-deposited is 15% chromium, 4% aluminum, 1% silicon, and the remainder nickel. The nominal composition of NASA-TRW VI-A superalloy is 7.5% cobalt, 6.0% chromium, 5.8% tungsten, 5.4% aluminum, 9.0% tantalum, 2.0% molybdenum, 1.0% titanium, 9.5% columbium, 0.40% rhenium, 0.5% hafnium, 0.1% zirconium, 0.13% carbon, 0.015% boron, and the remainder nickel. After 160 hours of testing in the very severe environment, the specimens showed no evidence of thermal fatigue crackling and the coating had completely protected the superalloy substrates from oxidation and erosion.

While several preferred embodiments of the invention have been described it is contemplated that various modifications may be made without departing from the spirit of the invention or the scope of the subjoined claims. By way of example, claddings of NiCrAl containing one or more of Si, Y, Mn and Th can be used. Also claddings of FeCrAl containing one or more of Y, Si, Mn and Ta can be used.

What is claimed is:

1. A coated article of manufacture comprising a superalloy substrate selected from the group consisting of nickel-base superalloys and cobalt-base superalloys, dispersion-strengthened alloys, composites, and directional eutectics,

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ductile, oxidation resistant metallic alloy layer covering said substrate, and an aluminide coating covering said metallic alloy layer.

2. An article of manufacture is claimed in claim 1 wherein the metallic alloy layer comprises a cladding.

3. An article of manufacture as claimed in claim 2 wherein the metallic alloy layer comprises a foil cladding.

4. An article of manufacture as claimed in claim 3 wherein the foil cladding is a NiCrAl alloy containing one or more elements selected from the group consisting of Si, Y, Mn, and Th.

5. An article of manufacture as claimed in claim 4 wherein the foil cladding is an alloy consisting essentially of from 15 to 25% chromium, 3 to 6% aluminum, 0.5 to 1.5% silicon, and the balance nickel.

6. An article of manufacture as claimed in claim 5 wherein the alloy consists essentially of about 18% chromium, about 4% aluminum, about 1% silicon, and the balance nickel.

7. An article of manufacture as claimed in claim 3 wherein the foil cladding is a FeCrAl alloy containing one or more elements selected from the group consisting of Y, Si, Mn, and Ta.

8. An article of manufacture as claimed in claim 7 wherein the foil cladding is an alloy consisting essentially of from 15 to 25% chromium, 3 to 6% aluminum, 0.1 to 1% yttrium, and the balance iron.

9. An article of manufacture as claimed in claim 8 wherein the alloy consists essentially of about 25% chromium, about 4% aluminum, 1% yttrium, and the balance iron.

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