United States Patent [19]

Felten

[11] **3,918,139**

[45] **Nov. 11, 1975**

[54] **MCrAlY TYPE COATING ALLOY**

[75] Inventor: **Edward J. Felten,** Cheshire, Conn.

[73] Assignee: **United Technologies Corporation,** Hartford, Conn.

[22] Filed: **July 10, 1974**

[21] Appl. No.: **487,074**

[52] **U.S. Cl.** **29/194;** 75/171

[51] **Int. Cl.**^{2} **B32B 15/04;** C22C 19/00

[58] **Field of Search** ...... 29/194; 75/171, 170, 134 F

[56] **References Cited**

UNITED STATES PATENTS

3,399,058	8/1968	Roush	75/170
3,589,894	6/1971	Roush	75/171
3,649,225	3/1972	Simmons	29/194
3,676,085	7/1972	Evans et al.	29/194
3,754,902	8/1973	Boone et al.	75/171
3,754,903	8/1973	Goward et al.	75/171

Primary Examiner—L. Dewayne Rutledge
Assistant Examiner—E. L. Weise
Attorney, Agent, or Firm—John D. Del Ponti

[57] **ABSTRACT**

There is described nickel, cobalt and nickel-cobalt alloy coating compositions having improved hot corrosion resistance. In particular, an improved MCrAlY type alloy coating composition consists essentially of, by weight, approximately 8–30 percent chromium, 5–15 percent aluminum, up to 1 percent reactive metal selected from the group consisting of yttrium, scandium, thorium and the other rare earth elements and 3–12 percent of a noble metal selected from the group consisting of platinum or rhodium, the balance being selected from the group consisting of nickel, cobalt and nickel-cobalt.

7 Claims, 5 Drawing Figures

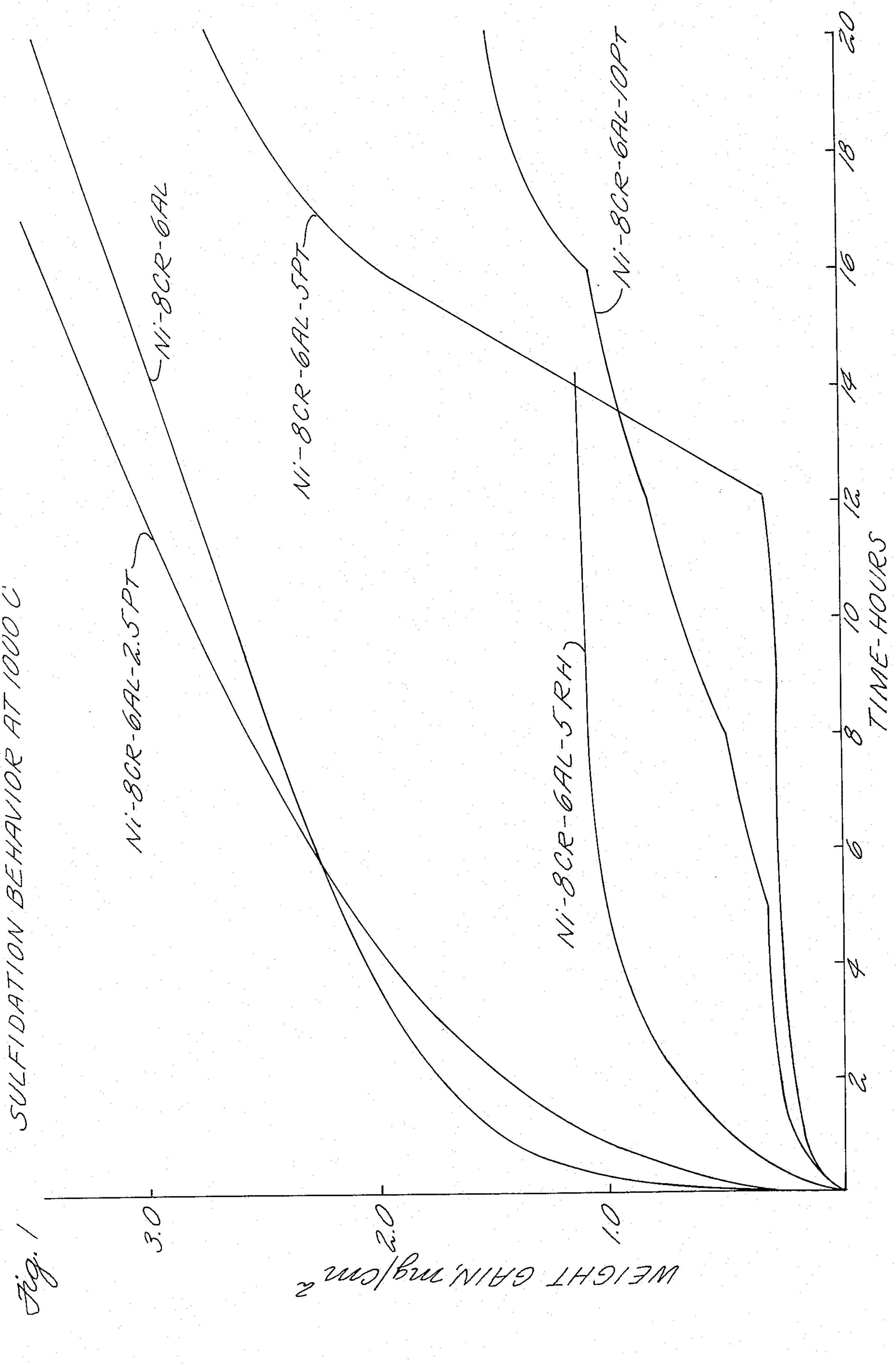

SULFIDATION BEHAVIOR AT 1000 C
Ni-8CR-6AL
Ni-8CR-6AL-2.5PT
Ni-8CR-6AL-5PT
Ni-8CR-6AL-10PT
Ni-8CR-6AL-5RH
WEIGHT GAIN, mg/cm2
3.0
2.0
1.0
TIME-HOURS
2
4
6
8
10
12
14
16
18
20

Fig. 1

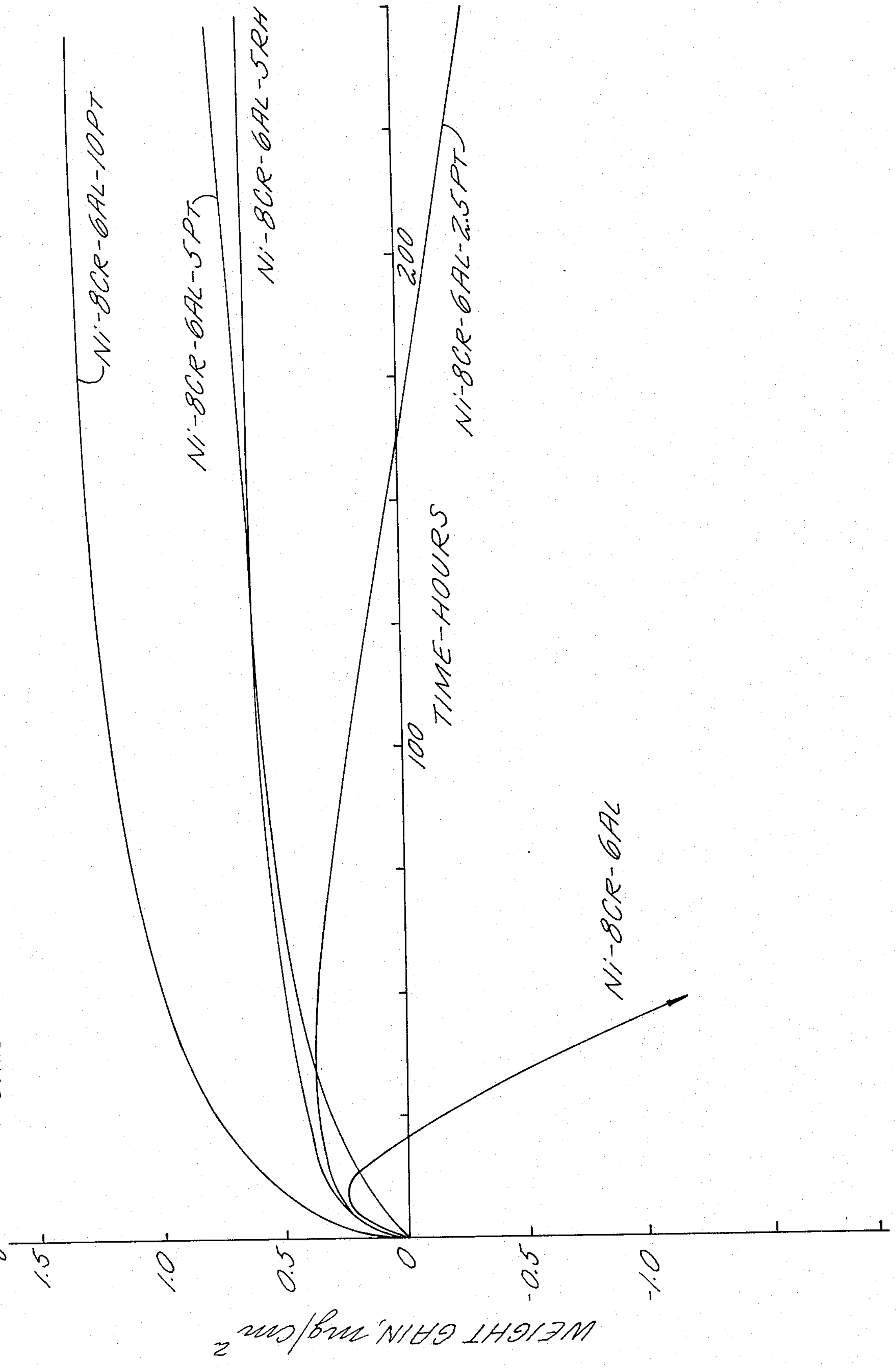
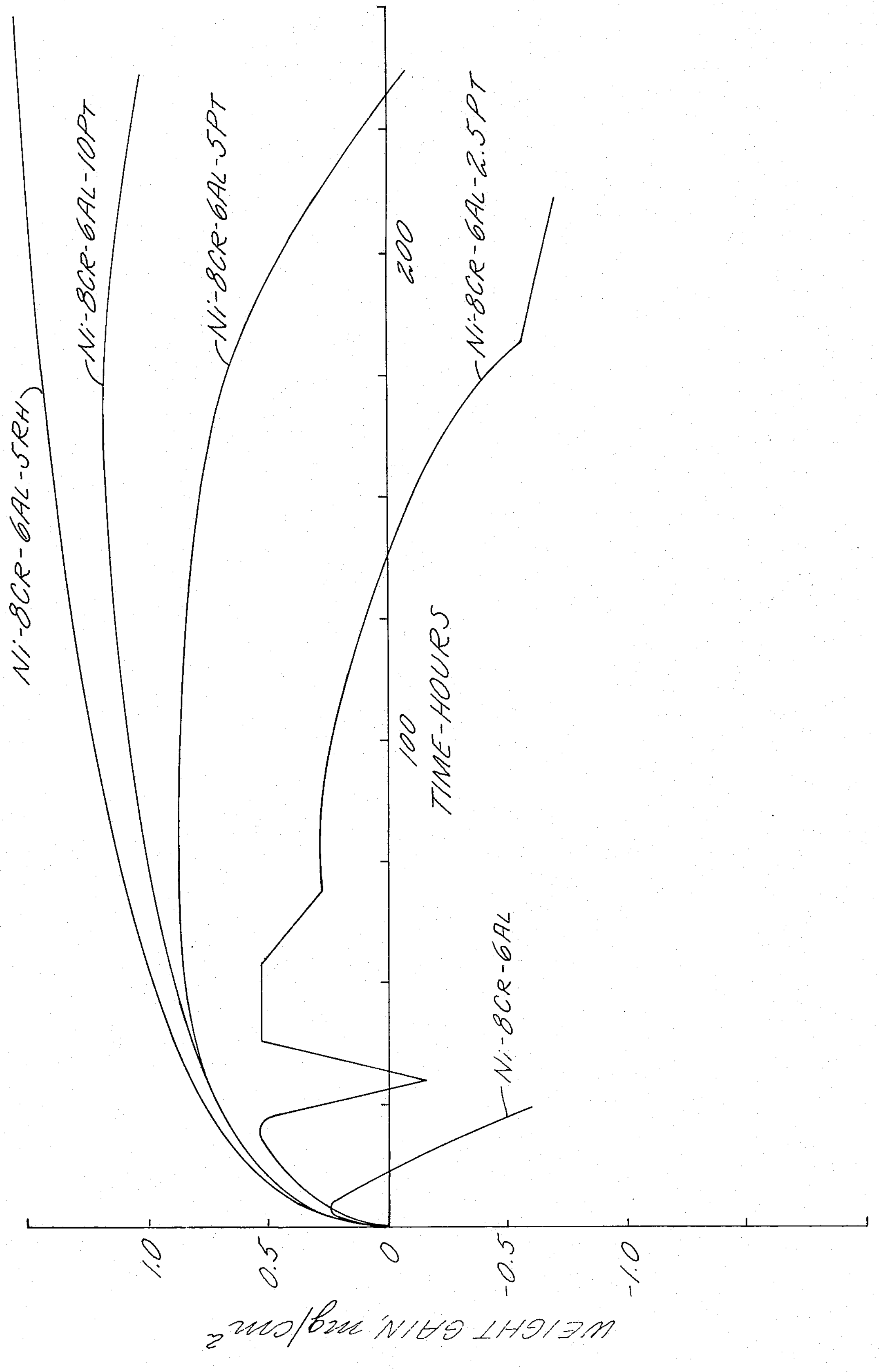

OXIDATION BEHAVIOR AT 1100°C IN AIR
Ni-8CR-6AL-10PT
Ni-8CR-6AL-5PT
Ni-8CR-6AL-5RH
Ni-8CR-6AL-2.5PT
Ni-8CR-6AL
TIME-HOURS
100
200
WEIGHT GAIN, mg/cm²
1.5
1.0
0.5
0
-0.5
-1.0

Fig. 2

Fig. 3



OXIDATION BEHAVIOR AT 1200°C IN AIR

Fig. 4

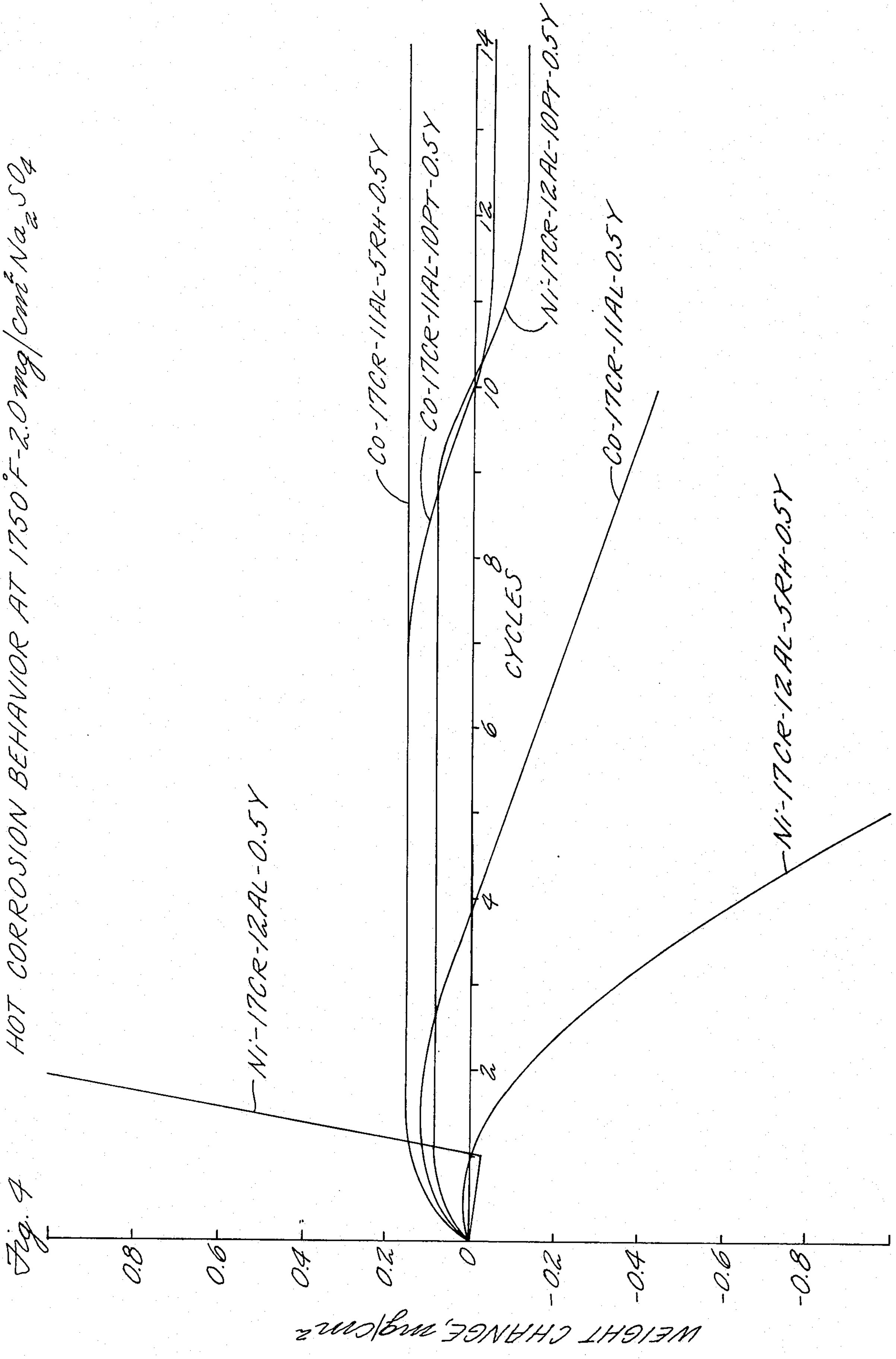
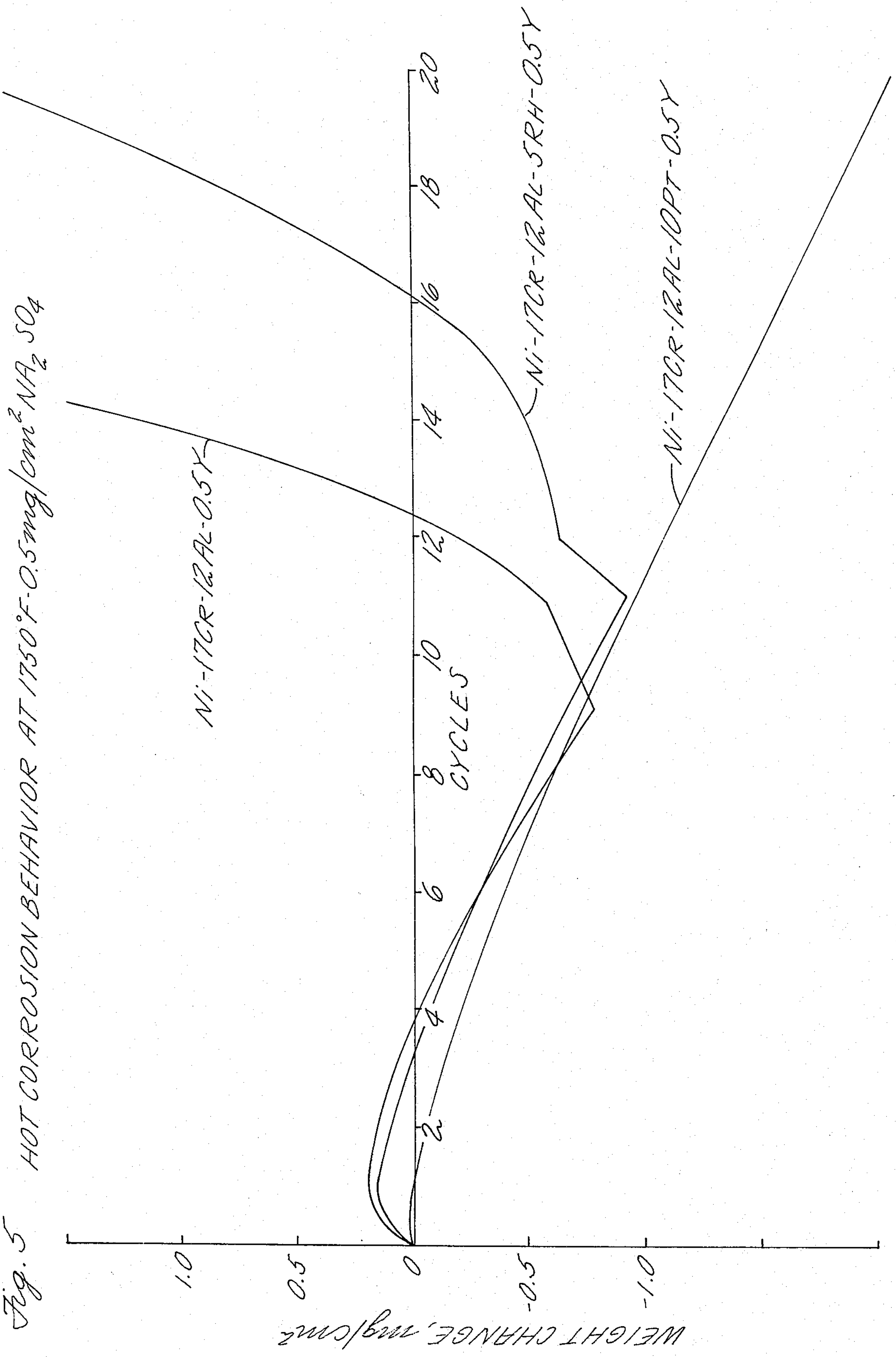

HOT CORROSION BEHAVIOR AT 1750°F-2.0 mg/cm² Na_2SO_4
WEIGHT CHANGE, mg/cm²
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
CYCLES
2
4
6
8
10
12
14
Ni-17CR-12AL-0.5Y
CO-17CR-11AL-5RH-0.5Y
CO-17CR-11AL-10PT-0.5Y
Ni-17CR-12AL-10PT-0.5Y
CO-17CR-11AL-0.5Y
Ni-17CR-12AL-5RH-0.5Y

Fig. 5


HOT CORROSION BEHAVIOR AT 1750°F-0.5mg/cm² NA₂ SO₄
WEIGHT CHANGE, mg/cm²
1.0
0.5
0
-0.5
-1.0
CYCLES
2
4
6
8
10
12
14
16
18
20
Ni-17CR-12AL-0.5Y
Ni-17CR-12AL-5RH-0.5Y
Ni-17CR-12AL-10PT-0.5Y

MCrAlY TYPE COATING ALLOY

BACKGROUND OF THE INVENTION

The present invention relates to alloys and more particularly to nickel, cobalt or nickel-cobalt coating alloys having improved hot corrosion resistance.

It is known that the modern day jet engine superalloys are susceptible to oxidation-erosion and hot corrosion at very high temperatures and that it is the usual practice to coat the superalloys with a composition different from and more oxidation-erosion and corrosion resistant than the substrate alloy.

In general, there are two primary types of coatings: (1) aluminide coatings, such as those described in the patent to Joseph U.S. Pat. No. 3,102,044 or the patents to Bungardt et al. U.S. Pat. No. 3,677,789 and U.S. Pat. No. 3,692,554 wherein aluminides are formed by a reaction with, or diffusion of a coating on, the substrate surface, and (2) overlay coatings such as those of the MCrAlY type, e.g., NiCrAlY described in the patent to Goward et al. U.S. Pat. No. 3,754,903, CoCrAlY described in the patent to Evans et al. U.S. Pat. No. 3,676,085, NiCoCrAlY described in the patent application to Hecht et al. Ser. No. 469,186 filed May 13, 1974 and FeCrAlY described in the patent to Talboom, Jr. et al. U.S. Pat. No. 3,542,530. Particularly useful overlay MCrAlY coatings are those consisting essentially of, by weight, approximately 8–30 percent chromium, 5–15 percent aluminum, up to 1 percent reactive metal selected from the group consisting of yttrium, scandium, thorium and lanthanum and the other rare earth elements, balance selected from the group consisting of nickel, cobalt and nickel-cobalt, preferably applied to a thickness of approximately 0.005–0.006 inch.

In contrast to the overlay coatings, the diffusion aluminide coatings are typically provided by reacting aluminum with the deoxidized surface of the article to be protected — the aluminide layer being formed as a barrier zone of varying component concentration with consumption of the substrate components. This aluminide layer in turn oxidizes to form the inert barrier oxide. In the Bungardt et al patents, a separate layer of metal from the platinum group is applied before the aluminum diffusion treatment. However, because of the complex nature of most of the contemporary alloys, and because the coating composition thereon is derived in part from the components of the substrate alloys, it is difficult to control the coating composition so as to cause the formation of a suitable barrier oxide. In addition, it is inherent in the diffusion technique that the coating formed is nonhomogeneous and, with respect to platinum group metal content for example, there appears a high concentration of the platinum group metal on the surface. The existence of such a gradient, of course, is disadvantageous since, with use, the coating diminishes in effectiveness as its composition changes.

Although the prior art coating compositions have represented improvements over various of their predecessor alloy compositions, the need for further improvements, particularly for example, in hot corrosion resistance, has remained.

SUMMARY OF THE INVENTION

The present invention contemplates alloy compositions and more particularly nickel, cobalt and nickel-cobalt coating alloy compositions having improved hot corrosion resistance. In particular, the present invention contemplates an improved MCrAlY type alloy coating composition consisting essentially of, by weight, approximately 8–30 percent chromium, 5–15 percent aluminum, up to 1 percent reactive metal selected from the group consisting of yttrium, scandium, thorium and the other rare earth elements, and 3–12 percent of a noble metal selected from the group consisting of platinum or rhodium, the balance being selected from the group consisting of nickel, cobalt and nickel-cobalt. As will be appreciated, the inclusion of the noble metal as an alloying ingredient results in a substantially uniform dispersion thereof throughout the composition and thus retains the homogeneity which is characteristic of MCrAlY type overlay coatings.

In a preferred embodiment, the reactive metal is yttrium and the noble metal is 5–10 percent platinum. In another embodiment, the reactive metal is yttrium and the noble metal is 5 percent rhodium.

BRIEF DESCRIPTION OF THE DRAWINGS

An understanding of the invention will become more apparent to those skilled in the art by reference to the following detailed description when viewed in light of the accompanying drawings, wherein:

FIG. 1 is a graph depicting the sulfidation behavior of various NiCrAl alloys at 1,000°C;

FIGS. 2 and 3 are graphs depicting the oxidation behavior of various NiCrAl alloys at 1,100°C and 1,200°C respectively, in air;

FIG. 4 is a graph showing the hot corrosion behavior of various CoCrAlY and NiCrAlY alloys at 1,750°F — 2.0 mg cm^{-2} Na_2SO_4; and

FIG. 5 is a graph showing the hot corrosion behavior of NiCrAlY alloys at 1,750°F — 0.5 mg cm^{-2} Na_2SO_4.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The alloys of the present invention exhibit markedly improved hot corrosion resistance and are considered particularly useful as coatings on the contemporary superalloys. The inventive alloys are in themselves corrosion resistant and do not depend for their protective effect upon a reaction with the substrate material. In addition, these alloys are uniform throughout their thickness and thus will exhibit their protective properties more continuously and consistently than do the aluminide coatings.

The desired results are obtained with a basic alloy containing approximately, by weight, 8–30 percent chromium, 5–15 percent aluminum, 5–10 percent platinum or rhodium, up to 1 percent reactive metal selected from the group consisting of yttrium, scandium, thorium and lanthanum and the other rare earth elements, balance nickel and/or cobalt. A preferred alloy composition utilizes 0.5 percent yttrium and 5–10 percent platinum.

It was surprising to find that the addition, as alloying ingredients, of specified amounts of platinum or rhodium to the MCrAlY type coatings would not only greatly enhance sulfidation resistance but also, even without the presence of the reactive metals (Y, Sc, Th, La and the other rare earths) which normally provide oxide adherence to the underlying substrate, would promote additional oxide adherence.

With respect to the processes whereby the alloy may be applied as a coating to the surface to be protected, the presence of platinum or rhodium to the coating alloy, because of the low vapor pressure of platinum or rhodium, generally precludes use of the vapor deposition technique. Other techniques are, however, efficacious to obtaining the properly composed coating. It is recognized, for example, that the coatings may be deposited by using a process involving simultaneous vapor deposition of the MCrAlY and sputter deposition of platinum or rhodium. As an alternative, the coatings may be accomplished by plasma spraying techniques.

A better understanding of the invention will result when viewed in light of the following examples:

EXAMPLE 1

Alloys of Ni-AlCr-6A with alloying additions of platinum and rhodium were made by the conventional arc melt-drop cast technique. Specimens of the compositions depicted in the graph of FIG. 1 had dimensions of 1 cm × 1 cm × ~0.2 cm and were subjected to hot corrosion tests as follows. Specimens of the alloys were spray coated with an aqueous solution of Na_2SO_4, dried and weighed. After achieving a coating of 0.5 mg cm^{-2} Na_2. SO_4, they were oxidized for 20 hours at 1,000°C in one atmosphere O_2 in a thermal balance. The specimen weight was recorded continuously as a function of time with the weight changes converted to weight gain per unit surface area and shown in FIG. 1.

As can be seen, the addition of 2.5 weight percent Pt did not significantly improve the performance of the Ni-8Cr-6Al alloy in this test. However a significant improvement in performance was obtained when 5 or 10 weight percent Pt was added. Specimens of the Ni-8Cr-6Al-5Rh alloy were approximately equivalent to that of the 10 Pt alloy.

EXAMPLE 2

Specimens were formed as in Example 1 to the compositions as shown in FIGS. 2 and 3. The specimens were subjected to high temperature cyclic oxidation tests and surprisingly, those containing platinum or rhodium, were found to have improved oxide adherence of the Al_2O_3 formed on the alloys. It can be seen that the alloys with 5 or 10 weight percent Pt are superior to the 2.5 weight percent Pt alloy which, in turn, is significantly better than the unmodified alloy. Oxide adherence on a Ni-8Cr-6Al-5Rh alloy at 1,200°C was found to be equivalent to that of the Ni-8Cr-6Al-10Pt alloy at the same temperature.

EXAMPLE 3

Alloy specimens having dimensions of 1 cm × 0.8 cm × 0.1–0.2 cm and compositions of Ni-17Cr-12Al-0.5Y, Ni-17Cr-12Al-5Rh-0.5Y, Ni-17Cr-12Al-10Pt-0.5Y, Co-17Cr-11Al-0.5Y, Co-17Cr-11Al-5Rh-0.5Y and Co-17Cr-11Al-10Pt-0.5Y were prepared, measured and weighed, then coated with 0.5–2.0 mg/cm^2 Na_2SO_4. They were then subjected to up to 14 cycles, each cycle consisting of oxidizing in air for 20 hours at 1,750°F, cooling to room temperature, washing and reweighing. The sequence was repeated to failure. The results obtained for one set of experiments at 1,750°F using 2 mg/cm^2 of salt is illustrated in FIG. 4. Although CoCrAlY is basically more resistant to hot corrosion than is NiCrAlY, it can be seen that additions of either Pt or Rh to either CoCrAlY, or NiCrAlY dramatically improve their hot corrosion resistance.

EXAMPLE 4

Erosion bars of Ni-17Cr-12Al-0.5Y, Ni-17Cr-12Al-5Rh-0.5Y, Ni-17Cr-12Al-5Pt-0.5Y and Ni-17Cr-12Al-10pt-0.5Y were evaluated in a cyclic hot corrosion burner rig at 1,750°F using 35 ppm of sea salt ingested in the fuel prior to combustion. Severe attack of the tip of both the NiCrAlY base composition and the rhodium modified composition occurred after 110 hours. Hot zone failures were observed between 300 and 400 hours for both these bars, the rhodium modified specimen surviving for a slightly longer time than the base composition. Although the rhodium modified composition showed little improvement over the base alloy in this test, the nature of its failure was unusual and rendered these results somewhat dubious and inconclusive. In contrast, the platinum modified compositions were found to be dramatically more resistant to hot corrosion than the base composition. For these compositions no sign of failure was observed up to 675 hours, when testing was terminated.

What has been set forth above is intended primarily as exemplary to enable those skilled in the art in the practice of the invention and it should therefore be understood that, within the scope of the appended claims, the invention may be practiced in other ways than as specifically described.

What is claimed is:

1. In a coating composition of the MCrAlY type wherein the coating composition consists essentially of, by weight, approximately 8–30 percent chromium, 5–15 percent aluminum, up to 1 percent reactive metal selected from the group consisting of yttrium, scandium, thorium and the other rare earth elements, balance selected from the group consisting of nickel, cobalt and nickel-cobalt, the improvement for increasing hot corrosion resistance which comprises 3–12 percent of a noble metal selected from the group consisting of platinum and rhodium as an alloying ingredient.

2. The invention of claim 1 wherein said reactive metal is yttrium.

3. The invention of claim 2 wherein said noble metal is 5–10 percent platinum.

4. The invention of claim 2 wherein said noble metal is 5 percent rhodium.

5. A coated article comprising a nickel-base or cobalt-base superalloy, and an overlay coating thereon of the MCrAlY type wherein the coating composition consists essentially of, by weight, approximately 8–30 percent chromium, 5–15 percent aluminum, up to 1 percent reactive metal selected from the group consisting of yttrium, scandium, thorium and the other rare earth elements, 3–12 percent of a noble metal selected from the group consisting of platinum or rhodium, balance selected from the group consisting of nickel, cobalt and nickel-cobalt, said platinum or rhodium being substantially uniformly dispersed throughout said overlay coating.

6. The invention of claim 5 wherein said reactive metal is yttrium.

7. The invention of claim 6 wherein said noble metal is 5–10 percent platinum.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,918,139
DATED : November 11, 1975
INVENTOR(S) : EDWARD J. FELTEN

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 14: "Ni-AlCr-6A" should read --Ni-8Cr-6Al--

Column 3, line 22: "$Na_2. SO_4$" should read --Na_2SO_4--

Column 4, lines 6-7: "Ni-17Cr-12Al-10pt-0.5Y" should read --Ni-17Cr-12Al-10Pt-0.5Y--

Signed and Sealed this

ninth **Day of** *March 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks