

Description

The present invention concerns a method for forming a gas phase aluminide coating on a nickel or cobalt base superalloy article.

Aluminide coatings provide protection against oxidation and corrosion degradation to nickel and cobalt base superalloy articles used in gas turbine engines. U.S. Patents which are indicative of the skill in the art relative to aluminide coatings include the following: 3,079,276, 3,276,903, 3,667,985, 3,801,353, 3,837,901, 3,958,047, 4,132,816, 4,142,023, 4,148,275 and 4,332,843. In general, aluminide coatings are formed by heating a powder mixture containing a source of aluminum, an activator, and an inert buffer or diluent, in the presence of the article to be coated. The article may either be embedded in the powder mixture (and the process is termed a "pack cementation" process) or the article is suspended in out-of-contact relation with the powder mixture (and the process is termed a "vapor phase" process).

The source of aluminum may be pure aluminum metal or it may be an alloy or intermetallic containing aluminum, such as Co_2Al_5 , as disclosed in US-A-4,132,816 to Benden et al.; US-A-3,958,047 to Baldi discloses the use of Ni_3Al as the source of aluminum; and US-A-4,332,843 to Ahuja discloses the use of Fe_2Al_5 . Activators which have been used in the aluminiding process generally include halides of alkali or alkaline earth metals. See, e.g., the aforementioned patent to Benden. Aluminum oxide is the typical diluent added to the powder mixture and controls the aluminum activity of the mixture. Aluminum oxide also prevents the powder mixture from sintering together during the coating process, as discussed in US-A-3,667,985 to Levine et al.

FR-A-1433672 discloses a method of forming an aluminide diffusion coating on a Ni-Co based superalloy article by heating the same in non oxidant atmosphere within a powder mixture containing a diffusing metallic material, an activator and a constituent capable of controlling and inhibiting the transfer of the metallic material from the powder mixture.

Three problems which have been prevalent, especially in the gas phase aluminiding processes, are the formation of cryolite, Na_3AlF_6 , on the surface of the coated article; the aggregation of "zipper oxides" on the original substrate surface; and the formation of oxides within the coating itself. Cryolite has been found to accelerate the rate of base metal degradation. While cryolite formation can sometimes be limited by using special aluminiding powder mixtures, the quality of the coatings produced by such mixtures is considered to be not as good as the quality of the coatings

produced by powder mixtures that result in cryolite formation. Oxides at the coating-substrate interface, and within the coating itself are undesired, since they also degrade coating properties. The former types of oxides can cause exfoliation of the coating; the latter type can act as fatigue initiation sites and sites for accelerated oxidation degradation.

Notwithstanding the advances made in the aluminiding field, researchers continue in their attempts to provide better coatings. Such coatings must have excellent resistance to oxidation and corrosion attack, and must be resistant to thermal fatigue. The present invention results from such effort.

The method of the present invention is defined as described in claim 1.

Improved gas phase aluminide coatings for articles of nickel and cobalt base superalloys are formed by heating a powder mixture, which consists essentially of cobalt aluminide, ammonium bifluoride, and an effective amount of chromium metal, mixture which is substantially free of aluminum oxide, and the article which is disposed in out-of-contact relation with the powder mixture, so that an outward diffusing aluminide coating is formed on the article. One powder mixture particularly useful in this invention consists of by weight percent, 5-20 $\text{NH}_4\text{F}\cdot\text{HF}$, 10-30 Cr, balance Co_2Al_5 . Elimination of aluminum oxide as a powder constituent has been found to dramatically improve the quality of the aluminide coating produced. In particular, there is no cryolite formation on the coating surface, and oxide contamination at the coating-substrate interface and within the coating itself is essentially eliminated. The use of ammonium bifluoride, $\text{NH}_4\text{F}\cdot\text{HF}$, results in a coating mixture with excellent "throwing power", i.e., the ability to coat internal surfaces of hollow gas turbine blades. Chromium is used as a buffer to control the aluminum activity, so that a thin, outward diffusing aluminide coating of 0.012-0.089 mm (0.0005-0.0035 inches) is formed. Such thin coatings have excellent resistance to thermal fatigue, and have resistance to oxidation degradation which is comparable to the best prior art aluminide coatings.

Other features of the invention will become apparent to those skilled in the art from the following description and accompanying drawing.

Figure 1 is a photomicrograph of a prior art, inward diffusing aluminide coating; and

Figure 2 is a photomicrograph of a prior art, outward diffusing aluminide coating; and

Figure 3 is a photomicrograph of the outward diffusing aluminide coating of the invention.

The invention is best understood by reference to the Figures. The inward diffusing prior art aluminide coating of Figure 1 is produced by a powder mixture which has a high aluminum activ-

en in the Figure, the coating is characterized by a three zone microstructure with considerable phase precipitation in the NiAl rich outer zone. While these types of coatings generally have good resistance to oxidation degradation, they range up to 0.10 mm (0.004 inches) thick. Such thick aluminide coatings are known to have relatively poor thermal fatigue resistance.

The prior art coating shown in Figure 2 was produced with a powder mixture which contained about 60% by weight aluminum oxide as the diluent. The resulting contamination is clearly evident. The powder mixture had a comparatively lower aluminum activity than the mixture which produced the coating in Figure 1. As a result, the substrate basis metal (which is nickel in Figure 2, since the substrate is a nickel base superalloy) has diffused outwardly while the aluminum in the powder mixture diffused inwardly. The majority of the oxide contamination in Figure 2 are zipper oxides, i.e., oxides at the original substrate interface. As noted above, these oxides can cause the coating to spall during service use.

As is seen in Figure 3, the coating of the invention is an outward diffusing coating like the coating in Figure 2, but is significantly cleaner than the Figure 2 coating. This factor, in addition to the nominal 0.05 mm (0.002 inch) coating thickness, results in excellent oxidation resistance as well as resistance to thermal fatigue cracking.

The coating of the invention is produced in the following manner. A powder mixture consisting essentially of, by weight percent, 5-20 $\text{NH}_4\text{F.HF}$, 10-30 Cr, balance Co_2Al_5 is prepared. A nickel base superalloy article is suspended above the mixture and enclosed in a sealed retort similar to that shown in US-A-4,148,275 to Benden et al. The retort is heated to 1038-1121°C (1,900-2,050°F), and after between about two and twelve hours, a coating similar to that shown in Figure 3 is produced. The coating has a clean, uncontaminated interface, a metallographically distinguishable two-zone outward diffusing aluminide microstructure, and is 0.012-0.089 (0.0005-0.0035 inches) thick, typically 0.038-0.063 mm (0.0015-0.0025 inches) thick. It contains about 20-35 weight percent aluminum, along with elements from the substrate.

A fluoride containing activator is preferred in the invention, since the use of such activators result in coating mixtures which have very good throwing power. Good throwing power is essential when a gas phase process is used to coat the internal surfaces of a hollow gas turbine engine blade. Ammonium bifluoride, $\text{NH}_4\text{F.HF}$, is the preferred activator although halides (most preferably fluorides) of alkali or alkaline earth metals may also be useful. Chromium is used as the diluent to control the activity of aluminum in the powder

mixture; without the presence of chromium, the mixture will be too active, and a thick, inward diffusing coating would be produced. The powder mixture is substantially free from aluminum oxide, which is widely used as the diluent in most prior art diffusion coating processes. It has been discovered that the presence of aluminum oxide in prior art coating mixtures is the apparent cause of the aforementioned undesired contamination (cryolite and entrapped oxides) which is typically observed in prior art gas phase aluminide coatings. According to the invention, aluminum oxide is removed from the powder mixture, which results in substantially cleaner (i.e., uncontaminated) coatings. While some small amounts of aluminum oxide (about 10% by weight, maximum) may be added to the powder mixture without causing an unacceptable amount of cryolite or oxides to form, the best aluminide coatings will be produced when the mixture is free of aluminum oxide. Powder mixtures containing no more than about 10 percent by weight of aluminum oxide are considered to be "substantially free" of aluminum oxide.

The preferred powder mixture of the invention consists of 5-20 $\text{NH}_4\text{F.HF}$, 10-30 Cr, up to about 10 Al_2O_3 , balance Co_2Al_5 . A preferred range is 7-17 $\text{NH}_4\text{F.HF}$, 13-23 Cr, balance Co_2Al_5 . The most preferred powder mixture is 12 $\text{NH}_4\text{F.HF}$, 18 Cr, balance Co_2Al_5 . When nickel base superalloy articles in out-of-contact relation to this most preferred mixture are heated to about 1080°C (1,975°F) for about four hours, the resultant coatings are typically 0.038-0.063 mm (0.0015-0.0025 inches) thick. They have comparable resistance to oxidation and corrosion attack as compared to prior art coatings, and better resistance to thermal fatigue cracking.

Claims

1. A method for forming a gas phase aluminide coating on a nickel or cobalt base superalloy article, comprising the steps of disposing the article in out-of-contact relation with a powder mixture and heating the article and powder mixture, said powder mixture consisting essentially of cobalt aluminide, ammonium bifluoride and an effective amount of chromium metal to form an outward diffusing aluminide coating, the powder mixture being substantially free of aluminum oxide.
2. The method according to claim 1 conducted to produce a coating of about 0.0127-0.089 mm (0.0005-0.0035 inches).
3. The method according to claim 1 wherein the powder mixture consists of, by weight percent, 5-20 $\text{NH}_4\text{F.HF}$, 10-30 Cr, balance Co_2Al_5 , and

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2. The method according to claim 1 conducted to produce a coating of about 0.0127-0.089 mm (0.0005-0.0035 inches).
3. The method according to claim 1 wherein the powder mixture consists of, by weight percent, 5-20 $\text{NH}_4\text{F}\cdot\text{HF}$, 10-30 Cr, balance Co_2Al_5 , and



heating the powder mixture to cause diffusion of aluminum into the article surface.

4. The method according to claim 3 wherein the powder mixture consists of 5-20 $\text{NH}_4\text{F}\cdot\text{HF}$, 10-30 Cr, balance Co_2Al_3 .
5. The method according to claim 3 wherein the powder mixture consists of 7-17 $\text{NH}_4\text{F}\cdot\text{HF}$, 13-23 Cr, balance Co_2Al_3 .
6. The method according to claim 3 wherein the powder mixture consists of 12 $\text{NH}_4\text{F}\cdot\text{HF}$, 18 Cr, 70 Co_2Al_3 .
7. The method according to claim 3 wherein the article and the powder mixture are heated at $1038^\circ\text{C} - 1121^\circ\text{C}$ ($1,900-2,050^\circ\text{F}$) for about 2-12 hours.

Patentansprüche

1. Verfahren zum Bilden eines Gasphasenaluminidüberzugs auf einem Nickel- oder Kobaltsuperlegierungsgegenstand, beinhaltend die Schritte Anordnen des Gegenstands in berührungsfreier Beziehung mit einem Pulvergemisch und Erhitzen des Gegenstands und des Pulvergemisches, wobei das Pulvergemisch im wesentlichen aus Kobaltaluminid, Ammoniumbifluorid und einer effektiven Menge an Chrommetall besteht, um einen Auswärtsdiffusionsaluminidüberzug zu bilden, wobei das Pulvergemisch im wesentlichen frei von Aluminiumoxid ist.
2. Verfahren nach Anspruch 1, durchgeführt, um einen Überzug von etwa 0,0127-0,089 mm (0,0005-0,0035 Zoll) herzustellen.
3. Verfahren nach Anspruch 1, wobei das Pulvergemisch, in Gewichtsprozent, aus 5-20 $\text{NH}_4\text{F}\cdot\text{HF}$, 10-30 Cr, Rest Co_2Al_3 , besteht, und Erhitzen des Pulvergemisches, um die Diffusion von Aluminium in die Gegenstandsfläche zu bewirken.
4. Verfahren nach Anspruch 3, wobei das Pulvergemisch aus 5-20 $\text{NH}_4\text{F}\cdot\text{HF}$, 10-30 Cr, Rest Co_2Al_3 besteht.
5. Verfahren nach Anspruch 3, wobei das Pulvergemisch aus 7-17 $\text{NH}_4\text{F}\cdot\text{HF}$, 13-23 Cr, Rest Co_2Al_3 , besteht.
6. Verfahren nach Anspruch 3, wobei das Pulvergemisch aus 12 $\text{NH}_4\text{F}\cdot\text{HF}$, 18 Cr, 70 Co_2Al_3 besteht.

7. Verfahren nach Anspruch 3, wobei der Gegenstand und das Pulvergemisch auf $1038^\circ\text{C} - 1121^\circ\text{C}$ ($1900-2050^\circ\text{F}$) für etwa 2-12 Stunden erhitzt werden.

Revendications

1. Procédé pour former un revêtement d'aluminium en phase gazeuse sur un article en superalliage à base de nickel ou de cobalt, comprenant les étapes consistant à disposer l'article hors de contact avec un mélange pulvérulent et à chauffer l'article et le mélange pulvérulent, ledit mélange pulvérulent étant essentiellement constitué par de l'aluminium de cobalt, du bifluorure d'ammonium et une quantité efficace de métal de chrome pour obtenir un revêtement en aluminium diffusant vers l'extérieur, le mélange pulvérulent étant essentiellement exempt d'oxyde d'aluminium.
2. Procédé selon la revendication 1, que l'on met en oeuvre pour obtenir un revêtement d'environ 0,0127-0,089 mm (0,0005-0,0035 pouce).
3. Procédé selon la revendication 1, dans lequel le mélange pulvérulent est constitué par, en pour cent en poids, 5-20 $\text{NH}_4\text{F}\cdot\text{HF}$, 10-30 Cr, le reste étant Co_2Al_3 , et dans lequel on chauffe le mélange pulvérulent pour provoquer la diffusion de l'aluminium à la surface de l'article.
4. Procédé selon la revendication 3, dans lequel le mélange pulvérulent est constitué par 5-20 $\text{NH}_4\text{F}\cdot\text{HF}$, 10-30 Cr, le reste étant Co_2Al_3 .
5. Procédé selon la revendication 3, dans lequel le mélange pulvérulent est constitué par 7-17 $\text{NH}_4\text{F}\cdot\text{HF}$, 13-23 Cr, le reste étant Co_2Al_3 .
6. Procédé selon la revendication 3, dans lequel le mélange pulvérulent est constitué par 12 $\text{NH}_4\text{F}\cdot\text{HF}$, 18 Cr, 70 Co_2Al_3 .
7. Procédé selon la revendication 3, dans lequel on chauffe l'article et le mélange pulvérulent à $1.038^\circ\text{C} - 1.121^\circ\text{C}$ ($1.900-2.050^\circ\text{F}$) pendant environ 2 à 12 heures.

