An article of manufacture having improved high temperature oxidation and corrosion resistance comprising:

(a) a superalloy substrate containing a carbide reinforcing phase, and

(b) a coating consisting of chromium, aluminum, carbon, at least one element selected from iron, cobalt or nickel, and optionally an element selected from yttrium or the rare earth elements.

8 Claims, 3 Drawing Figures
OXIDATION CORROSION RESISTANT SUPERALLOYS AND COATINGS

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautic and Space Act of 1958, Public Law 85–568 (72 Stat. 435 42 USC 2457).

BACKGROUND OF THE INVENTION

The present invention relates to an article of manufacture having improved high temperature oxidation and corrosion resistance comprising: (a) a superalloy substrate containing a carbide reinforcing phase, and (b) a coating consisting of chromium, aluminum, carbon, at least one element selected from iron, cobalt or nickel, and optionally an element selected from yttrium or the rare earth elements. Another embodiment of this invention comprises an aluminized overcoating of the coated superalloy. Still another embodiment of this invention comprises the method of making the article of manufacture described herein.

DESCRIPTION OF THE PRIOR ART

Carbide reinforced superalloys well-known to the art are employed widely in articles of manufacture employed in gas turbine engines including those which power aircraft engines. The superalloys which are carbide reinforced include conventionally cast, for example, nickel-base and cobalt-base superalloys, directionally solidified nickel-base and cobalt-base superalloys including eutectic alloys, as well as refractory alloys, etc. These alloys belong to a class of superstur superalloys which rely on carbides for at least a portion of their overall strength.

To further enhance the ability of superalloys in gas turbine applications, surface coatings generally are used to protect superalloy articles from deleterious high temperature oxidation, corrosion and erosion effects. Especially useful coating compositions (especially with directionally solidified eutectic compositions which have an aligned carbide reinforcing fibrous phase) are coating compositions consisting essentially of chromium, aluminum, at least one element selected from iron, cobalt or nickel, and optionally an element selected from yttrium or rare earth elements. Aluminization of the coatings further enhances the oxidation and corrosion resistance of the coated superalloy.

Although the above-described prior art coated superalloys have improved oxidation and corrosion resistance at elevated temperatures, including service temperatures where it is highly desirable to maintain the integrity of the substrates at temperatures approaching 1100° C., the prior art coated superalloys exhibit deficiencies in the form of a carbide depletion at the interface of the coating and the substrate as a result of diffusion of carbon from the substrate into the oxidation and corrosion resistant coatings significantly and deleteriously affects the phases which strengthen the superalloys.

DESCRIPTION OF THE INVENTION

This invention embodies an article of manufacture having improved high temperature oxidation and corrosion resistance comprising: (a) a superalloy substrate containing a carbide reinforcing phase, and (b) a coating consisting of chromium, aluminum, carbon, at least one element selected from iron, cobalt or iron, and optionally an element selected from yttrium or rare earth elements. Another embodiment of this invention comprises an aluminized overcoating of the coated superalloy. Still another embodiment comprises methods of preparing the aforesaid articles of manufacture.

Broadly, any of the superalloy compositions included within the Compilation of Chemical Compositions and Rupture Strengths of Superalloys described in the ASTM data series publication no. DS9E, which include carbon within the alloy and rely on carbides for at least a portion of their reinforcing strengths, e.g. (1) carbide reinforcement of grain boundaries in a monocarbide form, commonly referred to as MC, and (b) chromium carbide forms, commonly referred to as M_23C_6 and M_6C_6, (2) refractory metal carbides, etc., in platelet or fiber form strengthening grain interiors, aligned or nonaligned in accordance with the method of casting using conventional or directional solidification casting techniques, are included within the scope of our invention.

Representative generally useful superalloys include nickel-base alloys, iron nickel-base alloys, cobalt-base alloys or refractory metal alloys of the compositions summarized in Table I which follows:

<table>
<thead>
<tr>
<th>Table I</th>
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</thead>
<tbody>
<tr>
<td><strong>Nominal Composition, Weight %</strong></td>
</tr>
<tr>
<td><strong>Alloy(s)</strong></td>
</tr>
<tr>
<td>Nickel-Based Alloys</td>
</tr>
<tr>
<td>IN-739</td>
</tr>
<tr>
<td>MAR-M200(a)</td>
</tr>
<tr>
<td>MAR-M200(b)</td>
</tr>
<tr>
<td>Rene 80</td>
</tr>
<tr>
<td>Rene 95</td>
</tr>
<tr>
<td>TAZ-ZB(a)(b)</td>
</tr>
<tr>
<td>TRW VI A(a)</td>
</tr>
<tr>
<td>WAZ-20(a)(b)</td>
</tr>
<tr>
<td>Iron-Nickel-Based Alloys</td>
</tr>
<tr>
<td>Incoloy 802</td>
</tr>
<tr>
<td>S-590</td>
</tr>
<tr>
<td>Duraloy &quot;HOM-3&quot;(b)</td>
</tr>
<tr>
<td>Cobalt-Based Alloys</td>
</tr>
<tr>
<td>FSX-414(a)</td>
</tr>
<tr>
<td>FSX-410(a)</td>
</tr>
<tr>
<td>MAR-M509(a)</td>
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<tr>
<td>X-45(a)</td>
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TABLE I-continued

<table>
<thead>
<tr>
<th>Alloy(s)</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Nb</th>
<th>Ti</th>
<th>Al</th>
<th>B</th>
<th>Zr</th>
<th>Fe</th>
<th>Other</th>
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<tbody>
<tr>
<td>WC3015</td>
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<tr>
<td>Cb132M</td>
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<tr>
<td>SUS31</td>
<td>0.12</td>
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<td>0.03</td>
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<td>TZC</td>
<td>0.15</td>
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</tbody>
</table>

(a) Cast alloy
(b) Directionally solidified
(c) Maximum composition

The coating compositions consist essentially of chromium, aluminum, carbon, at least one element selected from iron, cobalt or nickel, and optionally an element selected from yttrium or the rare earth elements. The coating compositions can be described by the formulas:

\[ M CrAlY \]

in which \( M \) is base metal element, e.g. iron, cobalt or nickel. Any amount of base metal element, chromium, aluminum, and optionally yttrium or a rare earth element can be employed in accordance with the amounts well-known to those skilled in the art with regard to oxidation and corrosion resistance of the coating under superalloy service conditions. The function of the carbon in the coating is to avoid denudation of the carbide reinforcement in the coating adjacent to the superalloy interface surface, which has a very low vapor pressure, if contained in the coating or localized in the coating atmosphere with subsequent continuous oxidation of carbon at the coating atmosphere interface.

In general, presently preferred carbon stabilized MCrAlY coatings are of the compositions in weight percentages set out in the following table:

TABLE II

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>General</th>
<th>Preferred</th>
<th>More Preferred</th>
<th>Most Preferred</th>
</tr>
</thead>
<tbody>
<tr>
<td>chromium</td>
<td>10-50</td>
<td>10-30</td>
<td>15-25</td>
<td>19-21</td>
</tr>
<tr>
<td>aluminum</td>
<td>0-20</td>
<td>2-15</td>
<td>1-11</td>
<td>4-11</td>
</tr>
<tr>
<td>carbon</td>
<td>0.01-0.5</td>
<td>0.01-0.2</td>
<td>0.05-0.15</td>
<td>0.05-0.25</td>
</tr>
<tr>
<td>yttrium</td>
<td>0-1.5</td>
<td>0-1.5</td>
<td>0.05-0.25</td>
<td></td>
</tr>
</tbody>
</table>

The preferred aluminum content depends strongly on whether a duplex alumining treatment is to be given to the coated superalloy substrate. The carbon-saturated MCrAlY coating of our invention can be applied to the superalloy substrates by any means whereby carbon contained within the MCrAlY coating is uniformly distributed throughout the coating or localized in the coating adjacent to the superalloy interface surface, subject to the proviso that the carbon content of the coating be sufficient to completely saturate all of the MCrAlY phases in the coating, however, insufficient to form excessive amounts of carbides within the coating composition which deleteriously affect the oxidation and corrosion resistance of the coating under superalloy service conditions.

In general, the carbon-saturated MCrAlY coatings can be applied by any means such as (1) Physical Vapor Deposition (subject to the proviso that the carbon be deposited from a separate carbon source since carbon, which has a very low vapor pressure, if contained in the MCrAlY melt source would not be transferred to the superalloy substrate), (2) Chemical Vapor Deposition wherein organometallic compounds are employed wherein during decomposition of the organometallic compounds the carbon residue incorporated into the coating is present in amounts sufficient to saturate all phases of the coating, and (3) Carburization wherein the MCrAlY coating is saturated with carbon by pack carburizing or gas carburizing the PVD coating in a atmosphere containing carbon such as an atmosphere of carbon monoxide or carbon dioxide, etc. A preferred method of preparing the coated superalloy substrates of our invention employs a flame spraying procedure wherein an alloy wire or powder of a carbon saturated MCrAlY composition is deposited on a superalloy surface. Flame spraying or arc plasma spray deposition involves projecting liquid droplets onto a superalloy substrate by means of a high velocity gas stream. To minimize the oxygen content of the coating, deposition is often done in an inert atmosphere such as argon or vacuum. In general, methods which can be employed are well known to those skilled in the art and are described in the following publications:

As mentioned herebefore, the carbon saturated MCrAlY coated article of this invention can be further improved in oxidation and corrosion resistance by alumining the MCrAlY coated substrate by any method known to those skilled in the art, including Physical Vapor Deposition procedures described in detail in Vapor Deposition, edited by C. F. Powell et al., John Wiley & Sons, New York (1966).

Our invention is more clearly understood from the following description taken in conjunction with the accompanying figures described hereafter.

FIG. 1 is a photomicrograph of a transverse section (a) and a longitudinal section (b) of a photomicrograph of a directionally solidified nickel-base superalloy eutectic having a melt composition on a weight percent basis of Ni-3.3Co-4.4Cr-3.1W-5.4Al-5.6V-6.2Re-8.1Ta-0.54C. The photomicrograph section magnified (400X) shows an aligned monocarbide microstructure fiber formed during solidification comprising tantalum and vanadium carbides (Ta, V)C which can be identified as the darkest phase shown in the photomicrographs of both the transverse and longitudinal sections. The carbide fibers are approximately 1 μm in cross section and specimens coated using flame-spraying techniques.

The coating composition described and employed a nickel-20 chromium-10 aluminum-1.0 yttrium composition having an initial coating about 75 μm 0.1 yttrium-0.1 carbon and was used for coating over a section 0.3 centimeters long of the superalloy ingots which had been coated, thereby reducing it to a thick coating.

FIG. 2 is a photomicrograph (200X) of a NiTaC-13 alloy which had been coated, on a weight percent basis, with a carbon free nickel-20 chromium-10 aluminum-1.0 yttrium composition having an initial coating about 75 μm in thickness. FIG. 2(a) is the NiTaC-13 coated composition machined to remove approximately one-half of the coating over a section 0.3 centimeters long of the FIG. 2(b) 75 μm coating, thereby reducing it to a thickness of about 25 μm. The photomicrographs illustrate that after 119 hours of cyclic oxidation exposure at 1100°C the coated regions having about a 75 μm thickness exhibit approximately twice the carbide fiber denudation as the composition having a coating thickness of about 25 μm. This figure illustrates that the coating acts as a sink for carbon since the 75 μm thick coating shows approximately twice the fiber denudation as the 25 μm thick coating.

FIG. 3 is a photomicrograph (600X) of a longitudinal section of the alloy of FIGS. 1 and 2 which has been coated with a carbon saturated composition having a coating composition, on a weight percent basis, of nickel-20 chromium-5 aluminum-0.1 carbon-0.1 yttrium, and subsequently aluminized. FIG. 3(a) is a longitudinal cross-section of the as-deposited coating. FIGS. 3(b), (c) and (d) are longitudinal sections of cyclically oxidized coatings after 1000 hrs., 1500 hrs. and 2000 hrs., respectively. Cyclic oxidation consisted of one hour cycles wherein the coated alloy test specimens were exposed 50 minutes at 1100°C in a static air furnace and 10 minutes at 963°C in a forced-air cooler. The cross-sections of the carbon containing aluminized coatings and substrate illustrate that there is no carbon denudation as a result of introducing a sufficient amount of carbon to the MCrAlY coating to provide carbon in an amount sufficient to saturate the phases of the MCrAlY coating.

Our invention is further illustrated by the following example:
out our process, it will be apparent to those skilled in the
art that other changes and modifications can be made in
the particular embodiments of the invention described
which are within the full intended scope of the inven-
tion as defined by the appended claims.

We claim:

1. A method of improving the high temperature oxida-
tion and corrosion resistance and preventing loss of
strength of a carbide containing superalloy body, said
body containing a carbide reinforcing phase, com-
prising steps of: (a) coating the superalloy body with a
composition consisting essentially of chromium, alumi-
nium, carbon and at least one element selected from iron,
cobalt, or nickel, subject to the proviso that the coatings
contain an amount of carbon (1) sufficient to saturate
any solid state phases of the coating composition, (2)
sufficient to essentially equilibrate the chemical poten-
tial of carbon in the coating with that in the substrate
with minimum interaction, and (3) insufficient to form
substantial quantities of carbides in the coating composit-
ion.

2. The claim 1 method, wherein the coating contains
an element selected from yttrium or the rare earth ele-
ments.

3. The claim 2 method, further comprising: (b) sub-
jecting the coated body to an aluminizing overcoating
to further increase the oxidation and corrosion resis-
tance of the coating.

4. The claim 1 method, wherein the superalloy body
is selected from a wrought, conventionally cast, direc-
tionally solidified or powder formed nickel or a cobalt-
base superalloy body.

5. The claim 1 method, wherein the superalloy is a
directionally solidified multivariant eutectic comprising
a matrix of nickel or cobalt-base superalloy body, the
matrix being an aligned eutectic carbide reinforcing
phase.

6. The claim 5 method, wherein the eutectic carbide
reinforcing phase is selected from carbides of the group
consisting of tantalum and vanadium and their alloys
and mixture thereof embedded in the matrix.

7. The claim 1 method wherein the superalloy body
and the coating have initially essentially the same car-
bon chemical potential.

8. A method of improving the high temperature oxida-
tion and corrosion resistance and preventing loss of
strength of a carbide containing superalloy body, said
body containing a carbide reinforcing phase, com-
prising steps of: (a) coating the superalloy body with a
composition consisting essentially of chromium, alumi-
nium, carbon and at least one element selected from iron,
cobalt, or nickel, subject to the proviso that the coatings
contain an amount of carbon (1) sufficient to saturate
any solid state phases of the coating composition, (2)
sufficient to essentially equilibrate the chemical poten-
tial of carbon in the coating with that in the substrate
with minimum interaction, and (3) insufficient to form
substantial quantities of carbides in the coating composi-
tion; and (b) subjecting the coated body to an aluminizing
overcoating to further increase the oxidation and corrosion resistance of
the coating.

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