Abstract

A directionally solidified multivariant eutectic γ-γ' nickel-base superalloy casting having improved high temperature properties is provided comprising a two-phase eutectic structure consisting essentially of, on a weight percent basis, 6.0 to 9.0 aluminum, 5.0 to 17.0 tantalum, 0-10 cobalt, 0-6 vanadium, 0-6 rhenium, 2.0-6.0 tungsten, and the balance being nickel, subject to the proviso that the sum of the atomic percentages of aluminum plus tantalum is within the range of from 19-22, and the ratio of atomic percentages of tantalum to aluminum plus tantalum is within the range of from 0.12 to 0.23. Embedded within the γ nickel-base matrix are aligned eutectic γ' phase (primarily nickel-aluminum-tantalum) reinforcing fibers.
DIRECTIONALLY SOLIDIFIED EUTECTIC γ-γ' NICKEL-BASE SUPERALLOYS

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).

The present invention relates to multivariant eutectic γ-γ' nickel-base superalloy articles and compositions, and more particularly to such eutectic articles and compositions which include a γ phase nickel-base superalloy matrix reinforced with aligned γ' phase fibers. The present invention is characterized by the presence of 0-3 mol% vanadium, 0-3 mol% rhenium, 2.5-4.5 mol% tungsten and a basis of 6.5-8.1 mol% aluminum, 7.0-13.5 mol% tantalum, 0-10 mol% cobalt, balance nickel subject to the proviso that the atomic percent of aluminum and tantalum is 19-22 and the present preferred superalloy contains, on a weight ing primarily of nickel-aluminum-tantalum embedded in a directionally solidified to provide a fiber reinforced matrix.

The performance requirements for gas turbine engines such as those which power aircraft are constantly increasing, hence there is a continuing need for improved materials for gas turbine components, especially those which operate in high temperature environments. These improved materials are critical in affecting overall performance and allow designers to increase power generated, operating temperatures, component life, or combinations of these factors.

The development of nickel-base superalloys widely used for many years in the gas turbine engine art has reached a point where advances are based on nickel-base superalloy compositions which permit (a) the orientation of the eutectic phases, and (b) the inclusion of eutectic phase reinforcing members—such as fibers, which can be formed in situ during directional solidification of eutectic nickel-base superalloys. The identification of eutectic nickel-base superalloys that can be directionally solidified is desirable since such alloys when directionally solidified produce metallic composites containing aligned lamellae or fibers as a reinforcing phase dispersed in the matrix. In these directionally solidified eutectic alloy compositions, the highly desirable strength properties at high temperatures, i.e., greater than 1,000° C. (1,832° F.), are provided by the fiber reinforcing phase. Thus, in order to improve the high temperature stress rupture properties, it is desirable to identify the alloys, especially eutectic alloys which can be directionally solidified to provide a fiber reinforced superalloy matrix.

In accordance with the present invention, I have discovered a unidirectionally solidified anisotropic metallic casting having high temperature strength properties comprising a matrix of nickel-base superalloy—having an aligned reinforcing fibrous γ' phase consisting primarily of nickel-aluminum-tantalum embedded in the γ matrix—containing a weight percent basis of 6.0-9.0 aluminum, 5.0-17.0 tantalum, 0-10 cobalt, 0-6 vanadium, 0-6 rhenium, 2.0-6.0 tungsten and the balance being essentially nickel, subject to the proviso that the sum of the atomic percentages of aluminum plus tantalum is within the range of from 19-22, and the ratio of atomic percentages of tantalum to aluminum plus tantalum is within the range of from 0.12 to 0.23. A presently preferred superalloy contains, on a weight basis, 6.5-8.1 aluminum, 7.0-13.5 tantalum, 0-10 cobalt, 0-3 vanadium, 0-3 rhenium, 2.5-4.5 tungsten and the balance nickel subject to the proviso that the atomic percent of aluminum and tantalum is 19-22 and the ratio of tantalum to tantalum is 0.12-0.23. Since the γ and γ' phases are in equilibrium, all elements in the alloy are substantially present in both phases. I have found that these castings have substantial fiber densities and fiber volume fractions which significantly reinforce the castings, and that these castings have substantial stress-rupture properties at elevated temperatures.

My 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 longitudinal section of a directionally solidified eutectic illustrating the nickel-aluminum-tantalum rich fiber γ' phase in the nickel-base γ phase superalloy matrix. The alloy was directionally solidified at 0.79 inch/hr. (2.0 cm./hr.) and contains from 10 to 30 mm. long columnar grains with an interfiber spacing of 2 microns or less. The alloy melt composition on a weight percent basis is 74 nickel, 7.7 aluminum, 8.1 tantalum, 3 cobalt, 1.7 vanadium, 2.4 rhenium and 3.1 tungsten.

FIG. 2 is a photomicrograph of a transverse section of the alloy of FIG. 1.

As mentioned previously, the composite structures formed by directional solidification of the eutectic alloys of my invention consist of a nickel-base matrix γ phase with an aligned γ' fiber reinforcing phase containing mainly nickel, aluminum and tantalum embedded in the matrix. The γ Ni3(Al,Ta) compound is an ordered face-centered-cubic (fcc) L12 crystal structure with aluminum and tantalum at the corners of the unit cell and nickel at the face centers. Other elements are present in the γ' phase in minor amounts. In general, the matrix phase, γ', provides low temperature strength properties to the alloy below about 1,700° F., and the nickel-aluminum-tantalum reinforcing phase, γ', imparts high temperature strength properties to the alloy at temperatures above about 1,700° F. These high temperature strength properties may be most sensitively measured by stress-rupture tests well-known in the art, examples of which are set out in Table III hereinafter. Time-temperature parameters have been devised to assist in correlating and extrapolating stress-rupture data. One particularly useful stress-rupture parameter is the Larson-Miller parameter given by the equation

\[ P = \frac{T}{C} \log \frac{t}{10} \times 10^{13} \]

wherein \( P \) is the Larson-Miller parameter given by the equation

\[ P = \frac{T}{C} \log \frac{t}{10} \times 10^{13} \]

within which \( C \) is the Larson-Miller parameter and \( t \) is the time to rupture in hours, described in more detail in American Society of Engineers Transactions, 1952, volume 74, at pages 765-771. A plot of this parameter as a function of applied stress is a satisfactory way to report stress-rupture data. Another way of showing or illustrating the high temperature strength properties is in terms of time to rupture as a function of the temperature and the applied stress.

The directional solidification rate and the resultant morphology of the alloy is effected by the composition of the alloy. As defined herein and in the appended claims, the directional solidification (ds) rate is any rate at which the eutectic alloy may be solidified without formation of undesirable cell or dendrite structures.

In general, the maximum directional solidification rate of the γ-γ' fiber eutectics is a function of alloy composition for a fixed thermal gradient. In general, the solidification temperature gradient normally falls within the range of from about 60° to about 150° C. per centimeter, and the directional solidification rate falls within...
the range of from about one-forth in./hr. (0.64 cm./hr.) to about 1.57 in./hr. (4 cm./hr.) at 80° C. per centimeter of thermal gradient.

In order to provide the article of the present invention the nickel-base superalloys having the above-described careful balance of elements must be unidirectionally solidified to enable the Ni3 (Al, Ta)-rich γ' eutectic fibers to be formed simultaneously with and be bonded to the reinforced solid solution matrix. Such unidirectional solidification can be conducted by one or more of the many methods and using apparatus well-known and widely reported in the art as described by C. T. Sims et al., The Superalloys. Wiley & Sons (1972).

As stated hereinbefore, the nickel-base castings of the invention can have a melt composition consisting essentially of, on weight percent basis, 6.0–9.0 aluminum, 5.0–17.0 tantalum, 0–10 cobalt, 0–6 vanadium, 0–6 rhenium, 2.0–6.0 tungsten, 0–3 titanium, 0–6 niobium, the balance being nickel and incidental impurities, subject to the proviso that the sum of the atomic percentages of aluminum plus tantalum is within the range of from 19–22, and the ratio of atomic percentages of tantalum to aluminum plus tantalum is within the range of from 0.12 to 0.23. These proviso composition limitations describe superalloy casting on an atomic percentage and an atomic percentage ratio basis — having uncorrelated atomic percentages of aluminum plus tantalum, (Al+Ta), of approximately 19–22 percent and atomic percentage ratio of tantalum to aluminum plus tantalum, Ta/(Ta+Al), of approximately 0.12–0.23 — in order to define the aluminum-tantalum relationship essential to the fiber reinforced γ-γ' eutectic microstructure of the castings. In general, accordingly and illustratively, in my γ-γ' nickel-base superalloys as the weight percent of aluminum goes down the weight percent of tantalum goes up, e.g., 6.5 aluminum to 13.5 tantalum, and conversely as the weight percent of aluminum goes up the weight percent of tantalum goes down, e.g., 8.1 aluminum to 7 tantalum.

Further illustrative of the above defined alloy compositional interrelationship based on aluminum and tantalum are γ-γ' eutectic superalloy compositions which are suitable alternative compositions to the γ-γ' nickel base superalloys of FIGS. I and II are set out in Table I hereafter. The alternatives given in Table I can be routinely calculated by those skilled in the art accordingly.

<table>
<thead>
<tr>
<th>Alloy Composition of Alternative Alloy* Alternative Alloy** Composition No. 1 Composition No. 2</th>
<th>Alloy Composition of FIGS. I &amp; II</th>
<th>Alternative Alloy Composition</th>
<th>a/o (x) atm.wt. (5)</th>
<th>w/o (5)</th>
<th>a/o (x) atm.wt. (4)</th>
<th>w/o (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>74</td>
<td>1.260</td>
<td>73.90</td>
<td>4538.7</td>
<td>74.6</td>
<td>4538.7</td>
</tr>
<tr>
<td>C</td>
<td>7</td>
<td>0.285</td>
<td>16.70</td>
<td>4598.9</td>
<td>7.9</td>
<td>4023.2</td>
</tr>
<tr>
<td>Ti</td>
<td>6.1</td>
<td>0.03</td>
<td>2.65</td>
<td>419.8</td>
<td>7.2</td>
<td>803.2</td>
</tr>
<tr>
<td>V</td>
<td>1.7</td>
<td>0.03</td>
<td>2.00</td>
<td>101.9</td>
<td>1.7</td>
<td>101.9</td>
</tr>
<tr>
<td>W</td>
<td>2.4</td>
<td>0.13</td>
<td>75</td>
<td>139.7</td>
<td>2.4</td>
<td>139.7</td>
</tr>
<tr>
<td>N</td>
<td>3.1</td>
<td>0.13</td>
<td>75</td>
<td>183.9</td>
<td>3.2</td>
<td>183.9</td>
</tr>
<tr>
<td>Ni</td>
<td>74</td>
<td>1.260</td>
<td>73.90</td>
<td>4538.7</td>
<td>74.6</td>
<td>4538.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>w/o (1)</th>
<th>a/o (3)</th>
<th>w/o + atm.wt. (2)</th>
<th>a/o (x) atm.wt. (4)</th>
<th>w/o (5)</th>
<th>a/o (x) atm.wt. (4)</th>
<th>w/o (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>74</td>
<td>1.260</td>
<td>73.90</td>
<td>4538.7</td>
<td>74.6</td>
<td>4538.7</td>
<td>70.6</td>
</tr>
<tr>
<td>C</td>
<td>7</td>
<td>0.285</td>
<td>16.70</td>
<td>4598.9</td>
<td>7.9</td>
<td>4023.2</td>
<td>6.5</td>
</tr>
<tr>
<td>Ti</td>
<td>6.1</td>
<td>0.03</td>
<td>2.65</td>
<td>419.8</td>
<td>7.2</td>
<td>803.2</td>
<td>13.1</td>
</tr>
<tr>
<td>V</td>
<td>1.7</td>
<td>0.03</td>
<td>2.00</td>
<td>101.9</td>
<td>1.7</td>
<td>101.9</td>
<td>1.6</td>
</tr>
<tr>
<td>W</td>
<td>2.4</td>
<td>0.13</td>
<td>75</td>
<td>139.7</td>
<td>2.4</td>
<td>139.7</td>
<td>2.3</td>
</tr>
<tr>
<td>N</td>
<td>3.1</td>
<td>0.13</td>
<td>75</td>
<td>183.9</td>
<td>3.2</td>
<td>183.9</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Substitution of other γ' strengtheners, such as titanium and niobium can be made to partially replace Ta and/or Al. In any combination of the elements, Al, Ta, Ti and Nb, the sum of their atomic percents is within the range of 19–22%, and the amount of Al in the alloy is at least 14 atomic percent of the alloy. Substitution of Ti and/or Nb should not exceed 4 atomic percent of the alloy. This corresponds to approximately 3 weight percent Ti and 6 weight percent Nb. Accordingly, another embodiment of this invention includes nickel-base castings having a melt composition consisting essentially of, on a weight percent basis sufficient aluminum and tantalum to produce 19–22 atomic percent (Ta+Al+Ti+Nb) containing at least 14 atomic percent Al, in combination with 0–10 cobalt, 0–3 vanadium, 0–3 rhenium, 2.5–4.5 tungsten, 0–3 titanium, 0–6 niobium, the balance being nickel and incidental impurities.

Other elements, including carbon, boron and zirconium, may be added to the γ'-γ eutectics to accomplish the beneficial effects generally seen when included in generally known conventional superalloys. Accordingly, carbon can be added on a weight basis of from 0.01 to 0.1, preferably 0.025 to 0.075, to form an array of monocarbides positioned along grain boundaries to impart additional resistance to grain boundary failure.

Carbon in the alloy combines with tantalum in substantial amounts, such as 0.8 tantalum-0.2 vanadium carbide...
be further modified by conventional precipitation tech-
out my process, it will be apparent to those skilled in the
the particular embodiments of the invention described
art that other changes and modifications can be made in
modifications and changes that can be made in carrying
nickel-aluminum-tantalum composition containing a
complex cubic L12 crystal structure based on NiJAI can
aligned reinforcing y' phase consisting primarily of a
matrix of a y face centered cubic crystal structure nickel-base superalloy having embed-
ed in the y phase an aligned reinforcing fibrous y' phase consisting primarily of a nickel-aluminum-tan-
talum composition which is a complex cubic Ll2 crystal
structure based on Ni3Al.

2. The claim 1 article wherein the y phase contains
Ni3Al precipitate.
3. The claim 1 article wherein said casting consists
effectively of, on a weight percent basis, 6.0 to 9.0 al-
uminum, 5.0 to 17.0 tantalum, 0-10 cobalt, 0-6 vanadium,
0-6 rhenium, 2.0-6.0 tungsten, and the balance being nickel, subject to the proviso that the sum of the atomic
percentages of aluminum plus tantalum is within the
range of from 19-22; and the ratio of atomic percent-
ages of tantalum to aluminum plus tantalum is within the
range of from 0.12 to 0.23.
4. The claim 3 article containing 6.5-8.1 aluminum and
7.0-13.5 tantalum.
5. The claim 3 article containing, on a weight percent

TABLE II

<table>
<thead>
<tr>
<th>Example</th>
<th>Ni</th>
<th>Al</th>
<th>Ta</th>
<th>Co</th>
<th>V</th>
<th>Re</th>
<th>W</th>
<th>Alloy Morphology</th>
<th>Solidification Rate (cm./hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>77</td>
<td>6.8</td>
<td>6.7</td>
<td>3</td>
<td>1.5</td>
<td>2.2</td>
<td>2.8</td>
<td>Some aligned - (very limited)</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>75</td>
<td>7.4</td>
<td>7.6</td>
<td>3</td>
<td>1.7</td>
<td>2.3</td>
<td>3.0</td>
<td>γ dendritic</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>74</td>
<td>7.7</td>
<td>8.1</td>
<td>3</td>
<td>1.7</td>
<td>2.4</td>
<td>3.1</td>
<td>aligned γ-γ'</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>74</td>
<td>7.7</td>
<td>8.1</td>
<td>3</td>
<td>1.7</td>
<td>2.4</td>
<td>3.1</td>
<td>aligned γ-γ'</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>73.4</td>
<td>7.9</td>
<td>8.5</td>
<td>3</td>
<td>1.7</td>
<td>2.4</td>
<td>3.1</td>
<td>aligned γ-γ'</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>73.4</td>
<td>7.9</td>
<td>8.5</td>
<td>3</td>
<td>1.7</td>
<td>2.4</td>
<td>3.1</td>
<td>aligned γ-γ'</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>72.8</td>
<td>8.1</td>
<td>8.9</td>
<td>3</td>
<td>1.7</td>
<td>2.4</td>
<td>3.1</td>
<td>mostly γ dendritic, limited γ-γ' eutectic</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>70</td>
<td>8.1</td>
<td>8.9</td>
<td>3</td>
<td>1.7</td>
<td>2.4</td>
<td>3.1</td>
<td>γ' dendritic</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>72.8</td>
<td>8.1</td>
<td>8.9</td>
<td>3</td>
<td>1.7</td>
<td>2.4</td>
<td>3.1</td>
<td>5.5 no eutectic</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>71.7</td>
<td>8.4</td>
<td>9.4</td>
<td>3</td>
<td>1.7</td>
<td>2.5</td>
<td>3.3</td>
<td>γ' dendritic</td>
<td>2</td>
</tr>
</tbody>
</table>

*not part of the invention

TABLE III

Nickel-Base γ-γ' Superalloy Eutectics

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Ni3Al</th>
<th>Co V</th>
<th>Ta</th>
<th>Re</th>
<th>W</th>
<th>Temperature (°F)</th>
<th>Stress (psi)</th>
<th>Life (hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>73.4% Ni-7.9% Al-8.5% Ta-3% Co-1.7% V-2/4% Re-3.1% W</td>
<td>48,900</td>
<td>42,400</td>
<td>32</td>
<td>1100</td>
<td>14,000</td>
<td>320</td>
<td>55.5</td>
</tr>
</tbody>
</table>

*Solidification Rate (cm./hr.)

The multivariant eutectic γ-γ' castings containing a
matrix of a γ face centered cubic crystal structure nick-
elbase superalloy having embedded in the γ phase an
aligned reinforcing γ' phase consisting primarily of a
nickel-aluminum-tantulum composition containing a
complex cubic Ll2 crystal structure based on Ni3Al can
be further modified by conventional precipitation tech-
niques well known to those skilled in the art whereby
Ni3Al is precipitated in the γ phase.

Although the above examples have illustrated various
modifications and changes that can be made in carrying
out my 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.

I claim:
1. An article of manufacture having improved high
temperature properties comprising a unidirectionally
solidified anisotropic metallic multivariant eutectic
casting containing a matrix of a γ-face-centered-cubic
crystal structure nickel-base superalloy having embed-
ded in the γ phase an aligned reinforcing fibrous γ'
phase consisting primarily of a nickel-aluminum-tan-
talum composition which is a complex cubic Ll2 crystal
structure based on Ni3Al.
2. The claim 1 article wherein the γ phase contains
Ni3Al precipitate.
3. The claim 1 article wherein said casting consists
effectively of, on a weight percent basis, 6.0 to 9.0 al-
uminum, 5.0 to 17.0 tantalum, 0-10 cobalt, 0-6 vanadium,
0-6 rhenium, 2.0-6.0 tungsten, and the balance being nickel, subject to the proviso that the sum of the atomic
percentages of aluminum plus tantalum is within the
range of from 19-22; and the ratio of atomic percent-
ages of tantalum to aluminum plus tantalum is within the
range of from 0.12 to 0.23.
4. The claim 3 article containing 6.5-8.1 aluminum and
7.0-13.5 tantalum.
5. The claim 3 article containing, on a weight percent

5

(Ta0.3V0.2C). Additional elements commonly added to
superalloys for grain boundary strengthening and duc-
tility are zirconium and boron. These elements can have
a similar beneficial effect on behavior of my γ-γ' nickel-
base eutectics when added in amounts on a weight basis
up to 0.1 boron and 0.1 zirconium.

The elements vanadium, rhenium and tungsten which
are included in the alloy in amounts of preferably 1.3 to
1.7, 2.0 to 2.5, and 2.8 to 3.5, respectively, by weight,
function as γ phase solid solution strengtheners. Either
or both of the elements rhenium and tungsten can be
partially replaced by molybdenum on an atomic ratio of
about 1:1. A maximum of 3 weight percent (approximately 2 atom percent) can be employed as a substitute
for rhenium and/or tungsten. The substitution of mo-
lybdenum is primarily effective as an additional γ solid
solution strengthen and secondarily effective to steepen
the γ-γ' solvsus boundary, so that the volume fraction of γ' in the eutectic is less dependent on tem-
perature.

During the evaluation of the present invention, a
number of alloy compositions were evaluated. The follow-
ing Tables II and III list the compositions and test
results of some of the testing of such alloys. All percent-
ages in these tables and elsewhere in the specification
are percents by weight unless otherwise stated.

The elements vanadium, rhenium and tungsten which
are percents by weight unless otherwise stated.

Example Ni Al Ta Co V Re W Alloy Morphology

<table>
<thead>
<tr>
<th>Example</th>
<th>Composition Rate* (psi)</th>
<th>Temperature (°F)</th>
<th>Stress (psi)</th>
<th>Life (hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>73.4% Ni-7.9% Al-8.5% Ta-3% Co-1.7% V-2/4% Re-3.1% W</td>
<td>104,000</td>
<td>86,100</td>
<td>1100</td>
</tr>
</tbody>
</table>

*Solidification Rate (cm./hr.)

The claim 3 article containing, on a weight percent
basis, 0-0.1 carbon.

6. The claim 3 article containing, on a weight percent
basis, 0-0.01 boron.

7. The claim 3 article containing, on a weight percent
basis, 0-0.1 zirconium.

8. The claim 3 article containing, on a weight percent
basis, 0-3 niobium replacing tantalum and/or aluminum
on an atomic ratio of about 1:1.

9. The claim 3 article containing, on a weight percent
basis, 0-6 niobium replacing tantalum and/or aluminum
on an atomic ratio of about 1:1.

10. The claim 3 article containing, on a weight per-
cent basis, 0-3 molybdenum replacing rhenium and/or
tungsten on an atomic ratio of about 1:1.
11. The claim 1 article consisting essentially of, on a weight basis, 73.4 percent nickel, 7.9 percent aluminum, 8.5 percent tantalum, 3 percent cobalt, 1.7 percent vanadium, 2.4 percent rhenium, and 3 percent tungsten.

12. The claim 1 articles consisting essentially of, on a weight basis, 7.5-8.1 percent aluminum, 7.6-8.8 tantalum, 0-10 percent cobalt, 0-3 percent vanadium, 0-3 percent rhenium, 2.4-4.5 percent tungsten and the balance being nickel.

13. The claim 1 article wherein the article is characterized at a temperature of 1100°C by a stress rupture life at 14,000 psi of at least 280 hours.