NI-BASE SINGLE CRYSTAL SUPERALLOY WITH ENHANCED CREEP PROPERTY

Inventors: Hyun Uk Hong, Changwon-si (KR); Chang Yong Jo, Changwon-si (KR); In Soo Kim, Changwon-si (KR); Baig Gyu Choi, Changwon-si (KR)

Assignee: KOREA INSTITUTE OF MACHINERY & MATERIALS, Changwon-city (KR)

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ABSTRACT

The present invention provides Ni-base single crystal superalloy with good high-temperature property, particularly long creep life and excellent resistance to creep deformation, by adjusting content of Al and Ti that form a gamma prime ($\gamma'$), a major hardening phase of the Ni-base single crystal superalloy. The Ni-base single crystal superalloy comprise Co: 11.5~13.5%, Cr: 3.0~5.0%, Mo: 0.7~2.0%, W: 8.5~10.5%, Al: 3.5~5.5%, Ti: 2.5~4.5%, Ta: 6.0~8.0%, Re: 2.0~4.0%, Ru: 0.1~2.0% in Weight %, and the rest is Ni and other inevitable impurities. And composition ratio of Al/Ti is 0.7~2.2. In addition, the superalloy has a mixed structure of the $\gamma$ matrix and $\gamma'$ particles.
FIG. 1

Creep tests
950°C/355MPa

Creep Strain (%)

Time (hours)
NI-BASE SINGLE CRYSTAL SUPERALLOY WITH ENHANCED CREEP PROPERTY

CROSS REFERENCE TO RELATED APPLICATIONS


FIELD OF THE INVENTION

[0002] The present invention relates to Ni-base single crystal superalloy, particularly, Ni-base single crystal superalloy with enhanced creep resistance and creep rupture time at high temperature by adjusting content of elements that form gamma prime (γ'), a hardening phase.

BACKGROUND

[0003] Ni-base superalloys are widely used as materials for major parts like blades and vanes of gas turbines for aircraft engines and for power generation. The application of single crystal superalloy increased because of its excellent high temperature mechanical properties compared with conventionally cast polycrystalline superalloy and directionally solidified superalloy.

[0004] Single crystal superalloy is strengthened by the precipitates of intermetallic γ' (L1₂ structure), a hardening phase having ordered structure within a matrix, and its matrix reinforced by adding alloying elements like W, Mo, Re, etc.

[0005] However, as environmental issues like global warming are on the rise, the necessity to enhance efficiency of the gas turbines by increasing the operation temperature becomes a matter of big concern. Therefore, temperature capability and creep life of blades and vanes used in the most extreme environment among gas turbine parts are getting important. Accordingly, development of single crystal superalloy with better creep property at high temperature than prior art is becoming more important.

[0006] The generation of single crystal superalloy is classified by Re content, an alloying element; that is, the 1st generation contains no Re content, the 2nd generation contains 3% of Re, the 3rd generation contains 6% of Re, etc. Also, the 4th generation with Ru addition was recently developed. Although temperature capability and creep resistance at high temperature have been improved as the generation is updated, the price of superalloy also went up because of an increase in addition of expensive elements such as Re, Ru, etc. For this reason, CMSX-4 (U.S. Pat. No. 4,643,782), the 2nd generation single crystal alloy containing 3% of Re developed by Cannon Muskegon, U.S., is being most commonly used at the present time.

[0007] In order to satisfy the need of developing single crystal superalloy with excellent temperature capability and creep resistance, adjusting content of other alloying elements while minimizing expensive alloying elements is regarded as an effective alloying design method. In case of parts that are used at high temperature, creep resistance is also a very important factor to be considered for alloying design because deformed parts cannot be used properly as per their original purposes or lower efficiency although creep lifetime is important.

[0008] As mentioned above, solid solution hardening elements such as W, Mo, Re, etc. can be adjusted in order to improve creep property of superalloy. In addition to this, creep property can be also enhanced by adjusting Al or Ti content that forms γ', a hardening phase having ordered structure (L1₂ structure). It is necessary to study the latter because it can suppress price rise compared with the former that enhances creep property through solid solution hardening by adding expensive elements such as Re, etc.

SUMMARY OF THE INVENTION

[0009] Accordingly, the present invention aims to provide Ni-base single crystal superalloy with good high-temperature property, particularly long creep life and excellent resistance to creep deformation, by adjusting content of Al and Ti that form a gamma prime (γ'), a major hardening phase of the Ni-base single crystal superalloy.

[0010] Ni-base single crystal superalloy with good creep property in the present invention consists of Co: 11.5–13.5%, Cr: 3.0–5.0%, Mo: 0.7–2.0%, W: 8.5–10.5%, Al: 3.5–5.5%, Ti: 2.5–4.5%, Ta: 6.0–8.0%, Re: 2.0–4.0%, Ru: 0.1–2.0% in Weight %, and the rest is Ni and other unavoidable impurities. At this time, composition ratio of Al/Ti is 0.7–2.2. The above superalloy may have a mixed structure of the γ matrix and γ' particles.

[0011] According to the Ni-base single crystal superalloy with good creep property of the present invention, it is possible to obtain alloy with prolonged creep rupture life and significantly improved time to 1% Creep Strain representing resistance to creep deformation through increasing misfit, a difference of lattice constant between the γ matrix and γ' particles, and reducing stacking fault energy, by producing single crystal superalloy consisting of Co: 11.5–13.5%, Cr: 3.0–5.0%, Mo: 0.7–2.0%, W: 8.5–10.5%, Al: 3.5–5.5%, Ti: 2.5–3.5%, Ta: 6.0–8.0%, Re: 2.0–4.0%, Ru: 0.1–2.0% in Weight %, and the rest containing Ni and other unavoidable impurities.

[0012] The foregoing and other objects, features, aspects and advantages of the present invention will be more clearly understood from the following detailed description with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. 1 is a graph that shows creep life and variation of creep strain with time when creep tests are performed with Ni-base superalloy according to the present invention at the condition of 950°C/355 MPa.

[0014] FIG. 2 is a photo of microstructure observed with a TEM (Transmission Electron Microscope) after a creep experiment for Test Material 1, Comparative Test Materials 1 and 2 of the present invention.

DETAILED DESCRIPTION

[0015] Ni-base single crystal superalloy with good creep property will be explained in the following embodiment. The creep property here means resistance to creep deformation as well as creep rupture life that is essential to use superalloy at high temperature. The said Ni-base superalloy has the following major features.

[0016] Ni-base single crystal superalloy with good creep property in the present invention obtains high temperature strength by both precipitation hardening and solid solution hardening.
A hardening phase, γ', having ordered structure (L1₂ structure) forms by adding Al and Ti in the γ-phase matrix, and the matrix is reinforced by adding solid solution hardening elements like W, Mo, Re, Ru, etc. Particularly, the Ni-base single crystal superalloy in the present invention is characterized by maximizing creep property by changing stacking fault energy through increasing Ti content and decreasing Al content, and also characterized by more enhanced creep properties than commonly used alloy.

In order to get the Ni-base single crystal superalloy with good creep property in the present invention, master ingots are cast using vacuum induction melting process. Then, single crystal specimens are produced from each master ingot respectively by the Bridgman method. And then, microstructure consisting of two phases of γ and γ' can be obtained by applying heat treatment to the specimens.

[Composition of the Alloy]

The Ni-base superalloy in the present invention has the following composition for each element. The reason for limiting amounts of each element will be explained here. The below weight % is gained by converting the amount added to weight while defining the entire Ni-base alloy as 100. In order to make it easy, explanation of Ni and other inevitable impurities will be omitted.

(1) Cobalt (Co) : 11.5–13.5%

Cobalt influences solution treatment temperatures by changing γ' solidus, a major hardening phase of Ni-base superalloy, and γ solids, a matrix, in addition to solid solution hardening. It also improves high temperature corrosion resistance. Creep property becomes worse if Co content is less than 11.5%, while it is difficult to decide heat treatment conditions because the temperature range of solution treatment becomes narrow if Co content is more than 13.5%.

(2) Chrome (Cr) : 3.5–5.0%

Chrome improves corrosion resistance of superalloy, however, the amount of Chrome is limited because it may produce carbides or TCP (Topologically Close Packed) phases which are detrimental to creep behavior. Corrosion resistance becomes bad if Cr content is less than 3.5%, while more than 5.0% Cr content may lower creep property and create TCP phases that negatively influence mechanical properties in case of long exposure at high temperature.

(3) Molybdenum (Mo) : 0.7–2.0%

Molybdenum improves property of superalloy at high temperature as a solid solution hardening element. However, a large amount may increase density and create TCP phases. It is hard to expect solid solution hardening effect under 0.7%, while more than 2.0% increase the density.

(4) Tungsten (W) : 8.5–10.5%

Tungsten is an element that enhances creep strength by solid solution hardening. However, a large amount may increase density, and lower toughness, corrosion resistance, and phase stability. In addition, a possibility of casting defects like freckles increases at a time of single crystal and directional solidification. Accordingly, more than 8.5% Tungsten is added for improving high temperature strength while Tungsten content is limited to 10.5% in order to inhibit undesirable effects.

(5) Aluminum (Al) : 3.5–5.5%

Aluminum is an essential element to improve high temperature creep property because it is a constitutive element of γ', a major hardening phase of Ni-base superalloy. In addition, it improves oxidation resistance. However, creep strength lowers under 3.5% while mechanical property may become worse due to precipitation of excessive γ' phases in case of adding more than 5.5%. Although absolute quantity of Al is important, an association with Ti content, another γ' phase forming element, is also important.

(6) Titanium (Ti) : 2.5–4.5%

Titanium, like Aluminum, improves creep strength as a constitutive element of a γ' phase. Particularly, more than 2.5% should be added in order to enhance creep property because addition of Ti increases misfit and decreases stacking fault energy. However, the amount should be limited to 4.5% because excessive addition may reduce oxidation resistance and lower phase stability.

(7) Tantalum (Ta) : 6.0–8.0%

Tantalum improves creep strength by hardening ion resis. In addition, partitioning of tantalum to interdendritic region increases the density of interdendritic liquid, resulting in inhibition of freckles, one of casting defects. Therefore, more than 6.0% content is required. But if more than 8.0% are added, harmful δ phases can be precipitated.

(8) Rhenium (Re) : 2.0–4.0%

Rhenium, a solid solution hardening element, greatly contributes to improvement of creep property because its diffusivity is very low. In other words, Rhenium considerably improves resistance to creep deformation as well as creep life of superalloy. Yet, a large quantity lowers phase stability, increases density and raises the price, therefore, the present invention limited the amount of Rhenium to 2.0–4.0%.

(9) Ruthenium (Ru) : 0.1–2.0%

Ruthenium improves high temperature property by inhibiting creation of TCP phases through broadening the solid solution range of γ' phase and contributing to homogenization of segregation. Accordingly, in the present study Ruthenium is added to enhance resistance to creep deformation as well as creep life of superalloy. However, the amount is limited to 0.1–2.0% because the price of superalloy becomes expensive and the density increases if a large quantity of Ruthenium is contained.

The present inventions will be explained in more detail through the following embodiments.

[Table 1] shows the chemical composition of single crystal superalloy according to the present invention and alloy compared with the said superalloy.

According to [Table 1], Test Material 1 presents the composition of Ni-base alloy with 4.5 weight % of Al and 3.0 weight % of Ti added, while Test Material 2 shows a case with 5.0 weight % of Al and 2.5 weight % of Ti added. On the contrary, Comparative Test Material 1 is alloy with 5.5 weight % of Al and 1.0 weight % of Ti added, and Comparative Test Material 2 is CMSX-4 that is being most commonly used at the present time.
TABLE 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Al</th>
<th>Ti</th>
<th>Ta</th>
<th>Re</th>
<th>Ru</th>
<th>Hf</th>
<th>Al/Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
<td>1</td>
<td>11.59</td>
<td>3.09</td>
<td>0.98</td>
<td>8.54</td>
<td>4.45</td>
<td>3.00</td>
<td>6.92</td>
<td>2.98</td>
<td>0.98</td>
<td>0</td>
</tr>
<tr>
<td>Materials</td>
<td>2</td>
<td>11.57</td>
<td>4.07</td>
<td>1.02</td>
<td>8.59</td>
<td>5.02</td>
<td>2.51</td>
<td>7.01</td>
<td>2.97</td>
<td>0.97</td>
<td>0</td>
</tr>
<tr>
<td>Comparative</td>
<td>1</td>
<td>11.66</td>
<td>4.07</td>
<td>1.03</td>
<td>8.68</td>
<td>5.47</td>
<td>1.02</td>
<td>6.95</td>
<td>3.02</td>
<td>1.02</td>
<td>0</td>
</tr>
<tr>
<td>Test Materials</td>
<td>2</td>
<td>9.60</td>
<td>6.40</td>
<td>0.61</td>
<td>6.40</td>
<td>5.65</td>
<td>1.01</td>
<td>6.50</td>
<td>2.90</td>
<td>0</td>
<td>0.10</td>
</tr>
</tbody>
</table>

[0032] The above Test Materials and Comparative Test Materials were produced as follows. First of all, master ingots were cast using vacuum induction melting process. Then, single crystal specimens of 15 mm diameter and 180 mm length were produced by the Bridgman method with withdrawal rate of 4.0 mm/min. And then, microstructure consisting of two phases of γ and γ' can be obtained by applying heat to the specimens.

[0033] [Table 2] shows creep life and time to 1% creep strain when creep tests are conducted by applying stress of 355 MPa at 950°C with the above alloys. [FIG. 1] is a graph that shows variation of creep strain with time when creep tests are performed at the condition of 950°C/355 MPa.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Creep Rupture Time (Hour)</th>
<th>Time to 1% Creep Strain (Hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test Material 1</td>
<td>301.8</td>
<td>197.0</td>
</tr>
<tr>
<td>Test Material 2</td>
<td>270.2</td>
<td>151.9</td>
</tr>
<tr>
<td>Comparative Test Material 1</td>
<td>211.7</td>
<td>112.0</td>
</tr>
<tr>
<td>Comparative Test Material 2</td>
<td>125.1</td>
<td>57.0</td>
</tr>
</tbody>
</table>

[0034] As we know from [Table 2] and [FIG. 1], creep property of Ni-base alloy is greatly dependent on content of Al and Ti, gamma prime (γ') forming elements. That is, it is found that Test Material 1 with relatively higher Ti content and lower Al content shows significantly longer Creep Rupture Time and Time to 1% Creep Strain than other Test Materials or Comparative Test Materials. Of course, optimizing contents of other alloying elements is necessary in order to improve creep property by adjusting the gamma prime phase forming elements.

[0035] In the concrete, Creep Rupture Time of Test Materials 1–2 with relatively higher Ti content and lower Al content was 270.2–301.8 hours while Time to 1% Creep Strain was 151.9–197.0 hours. On the other hand, Comparative Test Materials 1–2 presented 123.1–211.7 hours of Creep Rupture Time and 57.0–112.0 hours of Time to 1% Creep Strain. Therefore, it was found that Test Material 1–2 of the present invention showed longer Creep Rupture Time and Time to 1% Creep Strain compared with Comparative Test Material 1–2.

[0036] FIG. 2 is a photo of microstructure observed with TEM (Transmission Electron Microscope) after a creep experiments for Test Material 1, Comparative Test Materials 1 and 2 of the present invention.

[0037] According to FIG. 2, although superdislocation is observed mainly inside of γ', a hardening phase, after the experiment in case of Comparative Test Materials 1 and 2, stacking fault is observed in Test Material 1. This is because formation of stacking fault becomes easier since stacking fault energy is lowered due to increase of Ti content. Dislocation mobility would be reduced by the dissociation of perfect dislocation into partial dislocations and stacking fault surrounded by them. Low dislocation mobility in γ' enhances the resistance to creep deformation. Therefore, it is found that creep property is improved by an increase of Ti content.

[0038] As the present invention may be embodied in several forms without departing from the characteristics thereof, it should also be understood that the above-described embodiments are not limited by any of the details of the foregoing description, therefore, various variations are possible by a person of ordinary skill in the pertinent art within the range of technical features of the present invention.

What is claimed is:
1. Ni-base single crystal superalloy with good creep property consisting of Co: 11.5–13.5%, Cr: 3.0–5.0%, Mo: 0.7–2.0%, W: 8.5–10.5%, Al: 3.5–5.5%, Ti: 2.5–4.5%, Ta: 6.0–8.0%, Re: 2.0–4.0%, Ru: 0.1–2.0% in weight %, and the rest containing Ni and other inevitable impurities, and composition ratio of Al/Ti is 0.7–2.2.
2. The Ni-base single crystal superalloy with good creep property according to claim 1, wherein the superalloy has a mixed structure of the γ matrix and γ' particles.