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(54) NICKEL-BASE SUPERALLOY

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(57) **ABSTRACT**

A nickel-base superalloy is characterized by the following chemical composition (details in % by weight): 7.7-8.3 Cr, 5.0-5.25 Co, 2.0-2.1 Mo, 7.8-8.3 W, 5.8-6.1 Ta, 4.9-5.1 Al, 1.3-1.4 Ti, 0.11-0.15 Si, 0.11-0.15 Hf, 200-750 ppm C, 50-400 ppm B, 0.1-5 ppm S, 5-100 ppm Y and/or 5-100 ppm La, remainder Ni and production-related impurities. The alloy is distinguished by very good casting properties, a high resistance to oxidation, and good compatibility with TBC layers applied to its surface.

NICKEL-BASE SUPERALLOY

[0001] This application is a Continuation of, and claims priority under 35 U.S.C. §120 to, International application number PCT/EP2005/055676, filed 1 Nov. 2005, and claims priority therethrough under 35 U.S.C. §119 to Swiss application number 1897/04, filed 18 Nov. 2004, the entireties of which are incorporated by reference herein.

BACKGROUND

[0002] 1. Field of Endeavor

[0003] The invention deals with the field of materials science. It relates to a nickel-base superalloy, in particular for the production of single-crystal components (SX alloy) or components with a directionally solidified microstructure (DS alloy), such as for example blades or vanes for gas turbines. However, the alloy according to the invention can also be used for conventionally cast components.

[0004] 2. Brief Description of the Related Art

[0005] Nickel-base superalloys of this type are known. Single-crystal components produced from these alloys have a very good material strength at high temperatures. This makes it possible, for example, to increase the inlet temperature of gas turbines, which boosts the efficiency of the gas turbine.

[0006] Nickel-base superalloys for single-crystal components, as are known from U.S. Pat. No. 4,643,782, EP 0 208 645 and U.S. Pat. No. 5,270,123, for this purpose contain alloying elements which strengthen the solid solution, for example Re, W, Mo, Co, Cr, as well as elements which form γ' phases, for example Al, Ta, and Ti. The level of high-melting alloying elements (W, Mo, Re) in the base matrix (austenitic γ phase) increases continuously with the increase in the temperature to which the alloy is exposed. For example, standard nickel-base superalloys for single crystals contain 6-8% of W, up to 6% of Re and up to 2% of Mo (details in % by weight). The alloys disclosed in the above-mentioned documents have a high creep strength, good LCF (low cycle fatigue) and HCF (high cycle fatigue) properties and a high resistance to oxidation.

[0007] These known alloys were developed for aircraft turbines and were therefore optimized for short-term and medium-term use, i.e., the load duration is designed for up to 20,000 hours. By contrast, industrial gas turbine components have to be designed for a load time of up to 75,000 hours.

[0008] By way of example, the alloy CMSX-4 from U.S. Pat. No. 4,643,782, when tested for use in a gas turbine at a temperature of over 1000° C., has a considerably coarsened γ' phase after a load time of 300 hours, and this phenomenon is disadvantageously associated with an increase in the creep rate of the alloy.

[0009] It is therefore necessary to improve the resistance of the known alloys to oxidation at very high temperatures.

[0010] A further problem of the known nickel-base superalloys, for example the alloys which are known from U.S. Pat. No. 5,435,861, is that in the case of large components, e.g., gas turbine blades or vanes with a length of more than 80 mm, the casting properties leave something to be desired. The casting of a perfect, relatively large directionally solidified single-crystal component from a nickel-base superalloy is extremely difficult, since most of these components have defects, e.g., small-angle grain boundaries, freckles, i.e., defects caused by a series of identically directed grains with a high eutectic content, equiaxed limits of variation, microporosity, etc. These defects weaken the components at high temperatures, and consequently the desired service life or operating temperature of the turbine are not achieved. However, since a perfectly cast single-crystal component is extremely expensive, the industry tends to permit as many defects as possible without the service life or operating temperature being adversely affected.

[0011] One of the most common defects is grain boundaries, which are particularly harmful to the high-temperature properties of the single-crystal items. Whereas in small components small-angle grain boundaries in relative terms have only a minor influence on the properties, they are highly relevant to the casting properties and oxidation properties of large SX or DS components at high temperatures.

[0012] Grain boundaries are regions with a high local disorder of the crystal lattice, since the neighboring grains collide in these regions, and therefore there is a certain misorientation between the crystal lattices. The greater the misorientation, the greater the disorder, i.e., the greater the number of dislocations in the grain boundaries which are required for the two grains to fit together. This disorder is directly related to the properties of the material at high temperatures. It weakens the material if the temperature rises to above the equicohesive temperature (=0.5×melting point in K).

[0013] This effect is known from GB 2 234 521 A. For example, in a conventional nickel-base single-crystal alloy, at a test temperature of 871° C., the fracture strength drops greatly if the misorientation of the grains is greater than 6°. This has also been confirmed in single-crystal components with a directionally solidified microstructure, and consequently the viewpoint has generally been that misorientations of greater than 6° are unacceptable.

[0014] It is also known from the above-referenced GB 2 234 521 A that enriching nickel-base superalloys with boron or carbon during a directional solidification produces microstructures which have an equiaxed or prismatic grain structure. Carbon and boron strengthen the grain boundaries, since C and B cause the precipitation of carbides and borides at the grain boundaries, and these compounds are stable at high temperatures. Moreover, the presence of these elements in and along the grain boundaries reduces the diffusion process, which is a primary cause of the grain boundary weakness. It is therefore possible to increase the misorientations to 10° to 12° yet still achieve good material properties at high temperatures. However, these small-angle grain boundaries have an adverse effect on the properties in particular of large single-crystal components formed from nickel-base superalloys.

[0015] Document EP 1 359 231 A1 describes a nickel-base superalloy which has improved casting properties and a higher resistance to oxidation than known nickel-base superalloys. Moreover, this alloy is, for example, particularly suitable for large gas turbine single-crystal components with a length of >80 mm. It has the following chemical composition (details in % by weight):

[0016] 7.7-8.3 Cr

[0017] 5.0-5.25 Co

[0018] 2.0-2.1 Mo

[0019] 7.8-8.3 W

[0020] 5.8-6.1 Ta

[0021] 4.9-5.1 Al

[0022] 1.3-1.4 Ti

[0023] 0.11-0.15 Si

[0024] 0.11-0.15 Hf

[0025] 200-750 ppm C

[0026] 50-400 ppm B

[0027] remainder nickel and production-related impurities. However, its compatibility with TBC (thermal barrier coating) layers, which are used in particular in the gas turbine sector to protect components exposed to particularly high thermal stresses, still needs improvement.

SUMMARY

[0028] One of numerous aspects of the present invention includes avoiding the abovementioned drawbacks of the prior art. Another aspect includes further improving the nickel-base superalloy which is known from EP 1 359 231 A1, in particular with a view to achieving better compatibility with TBC layers to be applied to this superalloy combined with equally good casting properties and a high resistance to oxidation compared to the nickel-base superalloy which is known from EP 1 359 231 A1.

[0029] According to yet another aspect of the present invention, a nickel-base superalloy embodying principles of the present invention is characterized by the following chemical composition (details in % by weight):

[0030] 7.7-8.3 Cr

[0031] 5.0-5.25 Co

[0032] 2.0-2.1 Mo

[0033] 7.8-8.3 W

[0034] 5.8-6.1 Ta

[0035] 4.9-5.1 Al

[0036] 1.3-1.4 Ti

[0037] 0.11-0.15 Si

[0038] 0.11-0.15 Hf

[0039] 200-750 ppm C

[0040] 50-400 ppm B

[0041] <5 ppm S

[0042] 5-100 ppm Y and/or 5-100 ppm La

remainder nickel and production-related impurities.

[0043] Some advantages of the invention are that the alloy has very good casting properties, a high resistance to oxidation at high temperatures, and is very compatible with TBC layers that are to be applied.

[0044] It is expedient if the alloy has the following composition (details in % by weight):

[0045] 7.7-8.3 Cr

[0046] 5.0-5.25 Co

[0047] 2.0-2.1 Mo

[0048] 7.8-8.3 W

[0049] 5.8-6.1 Ta

[0050] 4.9-5.1 Al

[0051] 1.3-1.4 Ti

[0052] 0.11-0.15 Si

[0053] 0.11-0.15 Hf

[0054] 200-300 ppm C

[0055] 50-100 ppm B

[0056] max 2 ppm S

[0057] 10-80 ppm Y and/or 10-80 ppm La

remainder nickel and production-related impurities.

[0058] An advantageous alloy according to the invention has the following chemical composition (details in % by weight):

[0059] 7.7 Cr

[0060] 5.1 Co

[0061] 2.0 Mo

[0062] 7.8 W

[0063] 5.8 Ta

[0064] 5.0 Al

[0065] 1.4 Ti

[0066] 0.12 Si

[0067] 0.12 Hf

[0068] 200 ppm C

[0069] 50 ppm B

[0070] 1 ppm S

[0071] 50 ppm Y

[0072] 10 ppm La

remainder nickel and production-related impurities.

[0073] This alloy is eminently suitable for the production of large single-crystal components, for example blades or vanes for gas turbines.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0074] The invention is explained in more detail below on the basis of an exemplary embodiment.

[0075] Nickel-base superalloys which are known from the prior art (comparison alloys CA1 to CA5) and the alloy-according to the invention A1, having the chemical composition listed in Table 1, were tested (details in % by weight):

TABLE 1

chemical composition of the alloys tested

Ni	CA1 (CMSX-11B) Remainder	CA2 (CMSX-6) Remainder	CA3 (CMSX-2) Remainder	CA4 (René N5) Remainder	CA5 (in accordance with EP 1359231A) Remainder	A1 Remainder
Cr	12.4	9.7	7.9	7.12	7.7	7.7
Co	5.7	5.0	4.6	7.4	5.1	5.1
Mo	0.5	3.0	0.6	1.4	2.0	2.0
W	5.1	—	8.0	4.9	7.8	7.8
Ta	5.18	2.0	6.0	6.5	5.84	5.8
Al	3.59	4.81	5.58	6.07	5.0	5.0
Ti	4.18	4.71	0.99	0.03	1.4	1.4
Hf	0.04	0.05	—	0.17	0.12	0.12
C	—	—	—	—	0.02	0.02
B	—	—	—	—	0.005	0.005
Si	—	—	—	—	0.12	0.12
Nb	0.1	—	—	—	—	—
Re	—	—	—	2.84	—	—
S	—	—	—	—	—	0.0001
Y	—	—	—	—	—	0.005
La	—	—	—	—	—	0.001

[0076] The alloy A1 is a nickel-base superalloy for single-crystal components, the composition of which is described herein. The alloys CA1, CA2, CA3, CA4 are comparison alloys which are prior art known under the designations CMSX-11B, CMSX-6, CMSX-2 and René N5. Inter alia, they differ from the alloy according to the invention primarily by virtue of the fact that they are not alloyed with C, B, Si, and Y and/or La. The comparison alloy CA5 is known from EP 1 359 231 A1 and differs from the alloy according to the invention in terms of the S, Y, and/or La content.

[0077] Carbon and boron strengthen the grain boundaries, in particular also the small-angle grain boundaries which occur in the <001> direction in SX or DS gas turbine blades or vanes made from nickel-base superalloys, since these elements cause the precipitation of carbides and borides at the grain boundaries, and these compounds are stable at high temperatures. Moreover, the presence of these elements in and along the grain boundaries reduces the diffusion process, which is a primary cause of the grain boundary weakness. This considerably improves the casting properties of long single-crystal components, for example gas turbine blades or vanes with a length of approx. 200 to 230 mm.

[0078] The addition of 0.11 to 0.15% by weight of Si, in particular in combination with Hf in approximately the same order of magnitude, significantly improves the resistance to oxidation at high temperatures compared to the previously known nickel-base superalloys CA1 to CA4.

[0079] Restricting the composition according to the invention to a sulfur content of <5 ppm produces very good properties, in particular good bonding of the TBC layer which has been applied to the surface of the superalloy, for example by thermal spraying. If the sulfur content is >5 ppm, this has an adverse effect on the TBC bonding, and the layer quickly flakes off in the event of fluctuating thermal stresses.

[0080] The addition of Y and/or La in the specified range (in each case 5 to 100 ppm), i.e., in total, that is to say Y+La, 10 to 200 ppm, if both elements are present produces very good bonding of the ceramic thermal barrier coating (TBC layer) which is to be applied.

[0081] The Y content of 50 ppm and the La content of 10 ppm specified for the alloy A1 is particularly advantageous, since A1 is particularly compatible with the TBC layers to be applied. Moreover, these two elements also increase the resistance to environmental influences. The addition of these elements in these low ranges stabilizes the aluminum/chromium oxide scale layer on the alloy surface and produces a significant resistance to oxidation. Y and La are oxygen-active elements which improve the bonding strength of the scale layer on the base material. The resistance to spalling during cyclic oxidation is the key factor for the stability of the TBC layer.

[0082] Table 2 in each case lists the number of cycles which it takes for the Al_2O_3 and other oxide layers formed to flake off under cyclic oxidation at 1050° C./1 h/air cooling to room temperature for the alloys listed in Table 1:

TABLE 2

number of cycles until spalling occurs

Alloy	Number of cycles until spalling occurs
CA1	<30
CA2	200
CA3	80
CA4	230
CA5	1500
A1	2500

[0083] The alloy according to the invention A1, compared to the alloys which are known from the prior art, has by far the highest number of cycles before the oxide layer flakes off. This implies a high stability of a TBC layer which is to be applied to the surface of the superalloy, for example by thermal spraying.

[0084] If, in other exemplary embodiments, by way of example, nickel-base superalloys with higher C and B contents (at most 750 ppm of C and at most 400 ppm of B) are selected, it is also possible for the components produced from these alloys to be cast conventionally, i.e., without them producing single crystals.

[0085] While the invention has been described in detail with reference to exemplary embodiments thereof, it will be apparent to one skilled in the art that various changes can be made, and equivalents employed, without departing from the scope of the invention. The foregoing description of the preferred embodiments of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and modifications and variations are possible in light of the above teachings or may be acquired from practice of the invention. The embodiments were chosen and described in order to explain the principles of the invention and its practical application to enable one skilled in the art to utilize the invention in various embodiments as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto, and their equivalents. The entirety of each of the aforementioned documents is incorporated by reference herein.

What is claimed is:

1. A nickel-base superalloy having the following chemical composition, in % by weight:

7.7-8.3 Cr

5.0-5.25 Co

2.0-2.1 Mo

7.8-8.3 W

5.8-6.1 Ta

4.9-5.1 Al

1.3-1.4 Ti

0.11-0.15 Si

0.11-0.15 Hf

200-750 ppm C

50-400 ppm B

<5 ppm S

5-100 ppm Y and/or 5-100 ppm La

remainder nickel and production-related impurities.

2. The nickel-base superalloy as claimed in claim 1, having the following chemical composition, in % by weight:

7.7-8.3 Cr

5.0-5.25 Co

2.0-2.1 Mo

7.8-8.3 W

5.8-6.1 Ta

4.9-5.1 Al

1.3-1.4 Ti

0.11-0.15 Si

0.11-0.15 Hf

200-300 ppm C

50-100 ppm B

max. 2 ppm S

10-80 ppm Y and/or 10-80 ppm La

remainder nickel and production-related impurities.

3. The nickel-base superalloy as claimed in claim 2, having the following chemical composition, in % by weight:

7.7 Cr

5.1 Co

2.0 Mo

7.8 W

5.8 Ta

5.0 Al

1.4 Ti

0.12 Si

0.12 Hf

200 ppm C

50 ppm B

1 ppm S

50 ppm Y

10 ppm La

remainder nickel and production-related impurities.

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