

# (11) **EP 1 837 411 A1**

(12)

## **EUROPEAN PATENT APPLICATION**

(43) Date of publication:

26.09.2007 Bulletin 2007/39

(51) Int Cl.: C22C 19/05 (2006.01)

(21) Application number: 07005969.6

(22) Date of filing: 22.03.2007

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE SI SK TR

**Designated Extension States:** 

AL BA HR MK YU

(30) Priority: 22.03.2006 JP 2006079447

(71) Applicant: Daido Tokushuko Kabushiki Kaisha Aichi (JP)

(72) Inventors:

 Kurata, Seiji Nagoya-shi, Aichi-ken (JP)

Ueta, Shigeki
 Nagoya-shi, Aichi-ken (JP)

Shimizu, Tetsuya
 Nagoya-shi, Aichi-ken (JP)

(74) Representative: Menges, Christian Alexander et al Diehl & Partner GbR.Augustenstr. 46

80333 Munich (DE)

## (54) Ni-based super alloy

(57) The present invention provides a Ni-based super alloy including, by mass %, C: 0.01 to 0.15%; Si: 1% or less; Mn: 1% or less; P: 0.02% or less; S: 0.01% or less; Co: less than 0.10%; Cr: 16 to 22 %; Mo: 4 to 10%;

W: 5% or less; Al: 1.2 to 2.5%; Ti: 2.4 to 4%; B: 0.001 to 0.05%; Zr: 0.01 to 0.5%; Fe: 1% or less; and a balance of Ni and inevitable impurities.

EP 1 837 411 A1

## Description

10

20

30

40

45

50

#### **FIELD OF THE INVENTION**

5 **[0001]** The present invention relates to a Ni-based super alloy.

## **BACKGROUND TO THE INVENTION**

**[0002]** Heretofore, as Ni-based super alloys, NCF751, NCF80A, and the like have been widely known. Such a kind of Ni-based alloys have been used for exhaust valve of automobile engines and the like where high-temperature strength is required.

**[0003]** Furthermore, JP-A-61-119640 discloses a Ni-based super alloy for exhaust valves comprising, by mass %, C: 0.01 to 0.15 %, Si: 2.0 % or less, Mn: 2.5 % or less, Cr: 15 to 25 %, Mo + 1/2 W: 0.5 to 5 %, Nb + Ta: 0.3 to 3 %, Ti 1.5 to 3.5 %, Al: 0.5 to 2.5 %, B: 0.001 to 0.02 %, Fe: 5 % or less, and the balance of substantially Ni.

**[0004]** In addition, JP-A-5-59472 discloses a Ni-based super alloy for exhaust valves comprising, by mass %, C: 0.16 to 0.54 %, Si: 0.5 % or less, Mn: 1.0 % or less, Co: 2.0 to 8.0 %, Fe: 12 % or less, Cr: 17.0 to 23.5 %, and one or two of Mo and W in the range of  $2.0 \le Mo + 1/2 W \le 5.5$ , which further containing Al: 1.0 to 2.0 % Ti: 2.5 to 5 % (provided that  $5.0 \le 1.8 \text{ Al} + \text{Ti} - 4\text{C} \le 6.0$ ), and one or two of B: 0.001 to 0.020 % and Zr: 0.005 to 0.15 %, and the balance of substantially Ni excluding impurities.

[0005] However, existing Ni-based super alloys have the following problems.

[0006] Namely, exhaust gas temperature of the conventional engines for automobiles are mainly around 800°C.

**[0007]** However, in recent years, in order to improve fuel costs and purify exhaust gases, there have been developed engines which operate near to the stoichiometric ratio. In such a kind of engines, the exhaust gas temperature reaches 900°C in some cases.

[0008] At such a temperature, in the existing Ni-based super alloys, mechanical properties at high temperature, such as tensile strength and fatigue strength, decrease in a large extent. Therefore, even when an exhaust valve is formed using conventional Ni-based super alloys, there arises a problem that necessary valve properties cannot be obtained and, as a result, engine performance cannot be sufficiently enhanced.

**[0009]** On the other hand, as a Ni-based super alloy which has excellent high-temperature strength, it is considered to use alloys containing Co in an amount of 12 to 14%, such as WASPALOY and UDIMET520.

**[0010]** However, since these Ni-based super alloys are poor in grindability, there arise problems that the life of a grindstone decreases and surface processing accuracy of products lowers. Furthermore, owing to a high Co content, material costs become very high.

## 35 SUMMARY OF THE INVENTION

**[0011]** Accordingly, an advantage of some aspects of the invention is to provide a relatively inexpensive Ni-based super alloy excellent in high temperature mechanical properties and grindability.

**[0012]** The present inventors have made eager investigation to examine the problem. As a result, it has been found that the foregoing objects can be achieved by the following Ni-based super alloys. With this finding, the present invention is accomplished.

**[0013]** The present invention is mainly directed to the following items:

- 1. A Ni-based super alloy comprising, by mass %: C: 0.01.to 0.15%; Si: 1% or less; Mn: 1% or less; P: 0.02% or less; S: 0.01% or less; Co: less than 0.10%; Cr: 16 to 22 %; Mo: 4 to 10%; W: 5% or less; Al: 1.2 to 2.5%; Ti: 2.4 to 4%; B: 0.001 to 0.05%; Zr: 0.01 to 0.5%; Fe: 1% or less; and a balance of Ni and inevitable impurities.
- 2. The Ni-based super alloy according to item 1, wherein Mo + 1/2W is 4 to 10%.
- 3. The Ni-based super alloy according to item 1 or 2, which further comprises at least one selected from the group consisting of Nb: 0.1 to 3%; and Ta: 0.1 to 3%.
- 4. The Ni-based super alloy according to any one of items 1 to 3, which further comprises at least one selected from the group consisting of Ca: 0.001 to 0.03%; Mg: 0.001 to 0.03%; and REM: 0.001 to 0.1%.
- 5. The Ni-based super alloy according to any one of items 1 to 4, which further comprises: Cu: 0.01 to 2%.
- 6. The Ni-based super alloy according to any one of items 1 to 5, which further comprises: V: 0.05 to 1 %.

<sup>55</sup> **[0014]** The Ni-based super alloy according to the invention has contents of specific ingredients in specific ranges. Therefore, the Ni-based super alloy according to the invention is excellent in mechanical properties such as tensile strength and fatigue strength even at a high temperature of 900°C.

[0015] In the present invention, the balance is Ni except for inevitable impurities such as oxide, sulfide, etc.

**[0016]** Moreover, in the Ni-based super alloy according to the invention, the content of Co is particularly limited to less than 0.10%. Therefore, it is excellent in grindability and the material costs become inexpensive as compared with WASPALOY and UDIMET520.

**[0017]** Therefore, in the case where the Ni-based super alloy according to the invention is used as a material for engine valves, it is easy to improve engine performance. Furthermore, the life of grindstone to be used at grinding of products is lengthened and also surface accuracy of the products can be improved.

**[0018]** In addition, the Ni-based super alloy according to the invention is also useful for turbine disks, blades, and the like, for example.

## 10 DETAILED DESCRIPTION OF THE INVENTION

**[0019]** The following will describe one embodiment of the invention in detail. With regard to the Ni-based super alloy according to the invention (sometimes referred to as "present alloy"), the contents of the specific ingredients fall within the ranges defined in the above and the balance comprises Ni and inevitable impurities. The reasons for defining the kinds of the specific ingredients and contents thereof are as follows. In this connection, the unit of the following contents is mass%.

(1) C: 0.01 to 0.15%:

[0020] C is an element which forms MC carbides in combination with Ti, Nb, and Ta and M<sub>23</sub>C<sub>6</sub> and M<sub>6</sub>C carbides in combination with Cr, Mo, and W, and contributes to prevent coarsening of grains and strengthening the grain boundary. In order to obtain the effects, the content of C is suitably 0.01% or more, preferably 0.03% or more.

**[0021]** On the other hand, when the content of C increases, the carbides increases and, for example, it becomes difficult to form a valve shape and toughness and ductility tend to lower. Therefore, the content of C is suitably 0.15% or less, preferably 0.10% or less.

**[0022]** According to an embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

(2) Si: 1% or less:

30

35

40

50

55

**[0023]** Si is an element which acts as a deoxidizer at dissolution and refining and may be incorporated according to need. Moreover, Si also contributes to improvement of oxidation resistance.

[0024] When the content of Si increases, toughness and workability tend to lower. Therefore, the content of Si is suitably 1% or less.

**[0025]** According to an embodiment, the minimal amount present in the alloy is at least 1/10 of the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

(3) Mn: 1% or less:

45 [0026] As the case of Si, Mn is an element which mainly acts as a deoxidizer and may be incorporated according to need.
[0027] When the content of Mn increases, oxidation resistance at high temperature, workability, and the like tend to lower. Therefore, the content of Mn is suitably 1 % or less.

**[0028]** According to an embodiment, the minimal amount present in the alloy is at least 1/10 of the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

(4) P: 0.02% or less:

**[0029]** P is an element which lowers hot workability. Since Ni is lowered in the present alloy, the range of temperature where hot working is possible is relatively narrow and hence it is desirable to secure hot workability as far as possible. Therefore, the content of P is suitably 0.02% or less.

**[0030]** According to an embodiment, the minimal amount present in the alloy is at least 1/10 of the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is 1.1 times the highest amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

(5) S: 0.01% or less:

[0031] As the case of P, S is an element which lowers hot workability. Therefore, the content of S is suitably 0.01 % or less.

**[0032]** According to an embodiment, the minimal amount present in the alloy is at least 1/10 of the smallest non-zero amount used in the examples of the developed alloys as summarized in Table .1. According to a further embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is 1.1 times the highest amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

(6) Co: less than 0.10%:

[0033] Co is a main element which lowers grindability. Moreover, it is also a main element which increases the material costs. Therefore, the content of Co is suitably less than 0.10%.

[0034] According to an embodiment, the minimal amount present in the alloy is at least 1/10 of the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is 1.1 times the highest amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

(7) Cr: 16 to 22 %:

[0035] Cr is an element which is necessary to improve the high temperature oxidation resistance and the corrosion resistance. In order to obtain the effect, the content of Cr is suitably 16% or more.

**[0036]** On the other hand, when the content of Cr increases, the  $\sigma$ -phase precipitates, so that toughness and high-temperature strength lower. Therefore, the content of Cr is suitably 22% or less.

[0037] According to an embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

(8) Mo: 4 to 10%:

**[0038]** Mo is an element which enhances high-temperature strength mainly through solid solution strengthening of the matrix. The content of Mo is suitably 4% or more to enhance strength at 900°C.

**[0039]** On the other hand, when the content of Mo increases, the material costs increase and also hot workability and oxidation resistance tend to lower. Therefore, the content of Mo is suitably 10% or less, preferably 7% or less.

**[0040]** According to an embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is 1.1 times the highest amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

(9) W: 5% or less:

[0041] As the case of Mo, W is an element which enhances high-temperature strength mainly through solid solution

4

20

10

35

30

45

40

50

strengthening of the matrix and may be incorporated according to need.

**[0042]** When the content of W increases, the material costs increase and also hot workability and oxidation resistance tend to lower. Therefore, the content of W is suitably 5% or less, preferably 3% or less.

**[0043]** According to an embodiment, the minimal amount present in the alloy is at least 1/10 of the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

**[0044]** In the present alloy, the above contents of Mo and W is preferably selected so that Mo + 1/2W falls within the range of 4 to 10%, more preferably within the range of 4 to 7%. This is because the resulting alloy is excellent in high-temperature strength and hot workability.

[0045] According to an embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is 1.1 times the highest amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

(10) AI: 1.2 to 2.5%:

[0046] Al is an important element for forming they'-phase which is effective for enhancing high-temperature strength in combination with Ni. When the content of Al decreases, the precipitation of the y'-phase becomes insufficient and high-temperature strength tends to be hardly secured. Therefore, the content of Al is suitably 1.2% or more.

**[0047]** On the other hand, when the content of Al increases, hot workability tends to lower. Therefore, the content of Al is suitably 2.5% or less, preferably 2.0% or less.

**[0048]** According to an embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

30 (11) Ti: 2.4 to 4%:

35

40

50

55

**[0049]** As the case of Al, Ti is an element for forming the y'-phase in combination with Ni. When the content of Ti decreases, the solid solution temperature of the  $\gamma$ '-phase lowers and a sufficient high-temperature strength tends to be not obtained. Therefore, the content of Ti is suitably 2.4% or more.

[0050] On the other hand, when the content of Ti increases, the  $\eta$ -phase (Ni<sub>3</sub>Ti) is apt to precipitate and thus there is observed a tendency that high-temperature strength and toughness deteriorate and hot workability lowers. Therefore, the content of Ti is suitably 4% or less, preferably 3.5% or less.

**[0051]** According to an embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

(12) B: 0.001 to 0.05%:

[0052] B is an element which contributes to the improvement of hot workability. Moreover, it is an element which segregates at grain boundary and is effective for strengthening the grain boundary and improving strength properties. In order to obtain the effects, the content ofB is suitably 0.001% or more.

**[0053]** On the other hand, when the content ofB increases, there is observed a tendency that the melting point drops and hot workability lowers. Therefore, the content ofB is suitably 0.05% or less.

[0054] According to an embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is 1.1 times the highest amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

(13) Zr: 0.01 to 0.5%:

[0055] Zr is an element which contributes to the improvement of hot workability. Moreover, it is an element which

segregates at grain boundary and is effective for strengthening the grain boundary itself and suppressing the formation of denuded zone of  $\gamma'$  in the vicinity of grain boundary to enhance strength at high temperature. In order to obtain the effects, the content of Zr is suitably 0.01 % or more.

[0056] On the other hand, when the content of Zr increases, there is observed a tendency that toughness lowers. Therefore, the content of Zr is suitably 0.5% or less.

[0057] According to an embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in

(14) Fe: 1% or less:

[0058] Fe is an element which lowers high-temperature strength and thus is desirably reduced as far as possible. Therefore, the content ofFe is suitably 1% or less.

[0059] According to an embodiment, the minimal amount present in the alloy is at least 1/10 of the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

[0060] The present alloy may further contain one or more elements selected from the following elements in addition to the aforementioned constitutional elements. The reasons for specifying the contents of these elements are as follows.

<1> At least one selected from the group consisting of: Nb: 0.1 to 3% and Ta: 0.1 to 3%:

[0061] Nb is an element which strengthens the γ'-phase in combination with Ni together with-Al. In order to obtain the effect, the content of Nb is suitably 0.1 % or more.

[0062] On the other hand, when the content of Nb increases, there is observed a tendency that hot workability lowers. Therefore, the content of Nb is suitably 3% or less, preferably 2% or less.

[0063] As the case of Nb, Ta is an element which strengthens the γ'-phase in combination with Ni together with Al. In order to obtain the effect, the content of Ta is suitably 0.1 % or more.

[0064] On the other hand, when the content of Ta increases, there is observed a tendency that hot workability lowers. Therefore, the content of Ta is suitably 3% or less, preferably 2% or less.

[0065] According to an embodiment, the minimal amount present in the alloy is at least 1/10 of the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is 1.1 times the highest amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

<2> At least one selected from the group consisting of Ca: 0.001 to 0.03%, Mg: 0.001 to 0.03%, and REM: 0.001 to 0.1%:

[0066] Ca, Mg, and REM are elements effective for improving hot workability. In order to obtain the effect, the contents of Ca, Mg, and REM are suitably 0.001% or more.

[0067] On the other hand, when the contents of Ca, Mg, and REM increase, there is observed a tendency that toughness lowers. Therefore, the content of Ca is suitably 0.03% or less. The content of Mg is suitably 0.03% or less. The content of REM is suitably 0.1 % or less.

[0068] According to an embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is 1.1 times the highest amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

<3> Cu: 0.01 to 2%:

[0069] Cu is an effective element for improving oxidation resistance. In order to obtain the effect, the content of Cu is suitably 0.01% or more.

[0070] On the other hand, when the content of Cu increases, there is observed a tendency that hot workability lowers.

6

10

20

25

30

35

40

45

50

Therefore, the content of Cu is suitably 2% or less.

**[0071]** According to an embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

<4> V: 0.05 to 1%:

**[0072]** As the cases of Mo and W, V is an element which contributes to solid solution strengthening of the matrix. Moreover, it has effects of forming MC carbides and stabilizing the carbides. In order to obtain the effects, the content of V is suitably 0.05% or more.

[0073] On the other hand, when the content of V increases, there is observed a tendency that toughness lower. Therefore, the content of V is suitably 1% or less.

**[0074]** According to an embodiment, the minimal amount present in the alloy is at least 1/10 of the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the minimal amount present in the alloy is the smallest non-zero amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is 1.1 times the highest amount used in the examples of the developed alloys as summarized in Table 1. According to a further embodiment, the maximum amount present in the alloy is the maximum amount used in the examples of the developed alloys as summarized in Table 1.

[0075] The following will describe one example of a process for producing the present alloy.

**[0076]** In order to obtain the present alloy, individual raw materials are weighed so as to obtain the aforementioned chemical composition and are melted to form an alloy ingot using a melting furnace such as an induction furnace. Thereafter, the resulting alloy ingot is subjected to hot forging or hot rolling, or the like according to need, whereby a desired shape can be obtained.

**[0077]** Furthermore, the resulting alloy ingot may be subjected to solution treatment, aging treatment, or the like according to need.

**[0078]** As the above solution treatment, there can be specifically exemplified, for example, a method of heating to a temperature of 950 to 1150°C and subsequently quenching.

**[0079]** As the temperature for the above aging treatment, there can be specifically exemplified, for example, a temperature of 500 to 1000°C, preferably 600 to 900°C.

**[0080]** The applications of the present alloy as described in the above are not particularly limited. As applications of the present alloy, there may be specifically exemplified engine valves, turbine disks, blades, heat-resistant springs, engine shafts, valves for ships, volts, and the like.

## **EXAMPLES**

20

30

35

45

50

55

[0081] The present invention is now illustrated in greater detail with reference to Examples and Comparative Examples, but it should be understood that the present invention is not to be construed as being limited thereto.

[0082] First, individual raw materials weighed so as to obtain the chemical composition shown in Tables 1 and 2 below were melted in an induction furnace and then cast to 50 kg each. Thereafter, the resulting each alloy ingot was subjected to hot forging and hot rolling at 1180°C to produce a round bar having a diameter of 16 mm.

**[0083]** Then, after held at 1050°C for 1 hour, the resulting each round bar was water-cooled to perform solution treatment and, after held at 750°C for 4 hours, it was air-cooled to perform aging treatment, thereby each test material being formed.

**[0084]** Thereafter, using each test material, a tensile test and a rotating bending fatigue test were carried out at room temperature and at 900°C.

**[0085]** In this connection, the tensile test at room temperature was carried out in accordance with JIS Z 2241 and the tensile test at 900°C was carried out in accordance with JIS G 0567.

**[0086]** In addition, the rotating bending fatigue test was carried out in accordance with JIS Z 2274 and the test was conducted at a rotation number of 3500 rpm at room temperature and at 900°C, respectively. Fatigue strength was obtained as the maximum skin stress when the number of cycles reached to 10<sup>7</sup> times before failure.

**[0087]** Then, a grinding test was carried out on each test material after aging. In the grinding test, using a test piece having an outer diameter of 25 mm and a ground part length of 300 mm, the piece was tested by a method of 5-paths grinding with a grindstone having an outer diameter of 600 mm at a grinding speed of 700 m/minute, a feeding speed of 30 mm/second, and a radial depth of 0.2 mm per path.

[0088] Then, grindability was evaluated by an abraded amount of the grindstone after grinding. Namely, the abraded amount of the grindstone with each test piece was represented by a ratio to the abraded amount with the test piece

according to Comparative Example 1, the amount being assigned as 100. The ratio was regarded as an index indicating the grindability.

**[0089]** Tables 1 and 2 shows chemical compositions of the Ni-based super alloys according to Examples and Comparative Examples and Table 3 shows test results of the N-based super alloys according to Examples and Comparative Examples.

 55
 45
 40
 35
 30
 25
 20
 15
 10

Table 1

									rable i								
	С	Si	Mn	Р	S	Со	Cr	Мо	W	Mo+ 1/2W	Al	Ti	В	Zr	Fe	Ni	Cu, V, Nb, Ta, Mg, Ca, REM
Example 1	0.04	0.47	0.62	0.005	0.004	0.02	19.7	5.19	-	5.19	1.64	3.51	0.003	0.02	0.42	Bal.	-
Example 2	0.11	0.23	0.44	0.003	0.006	0.07	16.3	4.81	3.16	6.39	1.24	3.68	0.005	0.04	0.38	Bal,	-
Example 3	0.06	0.45	0.31	0.002	0.003	0.08	20.5	6.41	-	6.41	1.74	2.52	0.016	0.23	0.81	Bal.	Ta:1.03
Example 4	0.05	0.21	0.13	0.004	0.007	0.08	19.52	4.28	-	4.28	1.41	3.24	0.004	0.06	0.31	Bal.	Nb:1.32
Example 5	0.09	0.56	0.27	0.003	0.006	0.01	18.6	4.92	-	4.92	2.42	3.03	0.026	0.14	0.28	Bal.	Ca:0.003
Example 6	0.01	0.31	0.97	0.008	0.003	0.03	21.3	5.17	1.04	5.69	1.83	3.17	0.007	0.08	0.73	Bal.	Cu:0.05, REM: 0.07
Example 7	0.05	0.64	0.38	0.007	0.002	0.09	20.3	6.83	-	6.83	1.46	3.97	0.013	0.48	0.52	Bal.	
Example 8	0.03	0.22	0.53	0.013	0.003	0.09	19.1	5.51	-	5.51	1.79	2.54	0.008	0.17	0.94	Bal.	Nb:1.24
Example 9	0.12	0.38	0.14	0.017	0.005	0.04	20.4	4.38	-	4.38	1.53	3.26	0.005	0.29	0.12	Bal.	-
Example 10	0.14	0.41	0.39	0.008	0.008	0.08	17.8	4.12	1.53	4.89	1.26	2.72	0.019	0.07	0.19	Bal.	Cu:0.18, Nb: 1.81
Example 11	0.08	0.96	0.83	0.007	0.002	0.02	21.8	7.91	-	7.91	2.25	2.43	0.044	0.32	0.32	Bal.	V:0.63, Mg: 0.007
Example 12	0.02	0.19	0.23	0.009	0.006	0.05	20.7	5.23	4.87	7.67	1.62	3.41	0.037	0.12	0.61	Bal.	Cu:1.92
Example 13	0.04	0.21	0.34	0.012	0.008	0.08	19.3	4.16	-	4.16	1.53	2.76	0.012	0.04	0.03	Bal.	-
Example 14	0.08	0.49	0.17	0.007	0.003	0.03	20.6	8.94	-	8.94	1.76	2.84	0.024	0.21	0.45	Bal.	-
Example 15	0.06	0.83	0.78	0.014	0.008	0.07	18.2	5.82	-	5.82	1.47	3.58	0.008	0.08	0.24	Bal.	-

 5
 5

 5
 45

 40
 35

 30
 25

 20
 15

 10
 5

 55
 5

Table 2

	С	Si	Mn	Р	S	Со	Cr	Мо	W	Mo + 1/2W	Al	Ti	В	Zr	Fe	Ni	Cu, V, Nb, Ta, Mg, Ca, REM
Example 1 Example	0.05	0.04	0.08	0.007	0.004	13.52	19.72	4.27	-	4.27	1.42	3.03	0.005	-	0.52	Bal.	-
Comparative Example 2	0.07	0.08	0.07	0.008	0.003	12.4	19.2	6.03	1.04	6.55	2.02	2.98	0.032	-	0.03	Bal	-
Comparative Example 3	0.06	0.14	0.08	0.003	0.006	0.08	20.3	5.24	-	5.24	1.17	2.31	-	-	0.58	Bal.	-
Comparative Example 4	0.04	0.06	0.07	0.004	0.005	0.04	15.48	0.08	-	0.08	1.18	2.32	-	-	7.26	Bal.	Nb:1.03
Comparative Example 5	0.05	0.08	0.05	0.002	0.003	1.02	19.43	0.06	-	0.06	1.43	2.26	-	-	1.53	Bal.	-

Table 3

	Properties at F	Room-temperature	Propert	Onice de hilitar / alamania a af	
	Tensile strength (MPa)	Fatigue strength at 10 <sup>7</sup> times (MPa)	Tensile strength (MPa)	Fatigue fatigue Fatigue strength at 10 times (MPa)	Grindability (abrasion of grindstone)
Example 1	1346	416	512	257	72
Example 2	1317	403	504	273	63
Example 3	1303	424	508	267	52
Example 4	1321	407	518	261	43
Example 5	1348	414	523	243	68
Example 6	1305	408	531	268	62
Example 7	1343	401	527	281	58
Example 8	1302	426	503	273	48
Example 9	1318	413	508	271	59
Example 10	1301	425	513	276	51

(continued)

	Properties at F	Room-temperature	Propert	Ovindahility (abvasion of	
	Tensile strength (MPa)	Fatigue strength at 10 <sup>7</sup> times (MPa)	Tensile strength (MPa)	Fatigue fatigue Fatigue strength at 10 times (MPa)	Grindability (abrasion of grindstone)
Example 11	1324	403	524	259	48
Example 12	1316	407	519	251	62
Example 13	1323	418	528	273	57
Example 14	1314	406	514	264	49
Example 15	1309	413	516	257	53
Comparative Example 1	1314	452	526	306	100
Comparative Example 2	1468	439	543	316	107
Comparative Example 3	1008	362	453	121	92
Comparative Example 4	1310	404	415	107	62
Comparative Example 5	1179	368	287	82	47

**[0090]** The following are found from Tables 1 to 3. Namely, the Ni-based super alloys according to Comparative Examples 1 and 2 particularly have an extremely high Co content. Therefore, it is found that they are poor in grindability. Moreover, since they contain a large amount of expensive Co, the material costs thereof are relatively high.

[0091] On the other hand, the Ni-based super alloys according to Comparative Examples 3 to 5 has a reduced Co content but the contents of  $\gamma$ -phase-forming elements such as A1 and Ti are low. Furthermore, the Ni-based super alloys according to Comparative Examples 4 and 5 has an extremely low contents of solid solution strenghtening elements such as Mo and W and the content of Fe decreasing high-temperature strength is extremely high. For these reasons, it is found that the Ni-based super alloys according to Comparative Examples 3 to 5 are poor in mechanical properties at high temperature.

[0092] However, in the Ni-based super alloys according to Examples 1 to 15, the contents of the specific ingredients fall within specific ranges. Therefore, the Ni-based super alloys according to Examples 1 to 15 are excellent in mechanical properties such as tensile strength and fatigue strength even at such a high temperature of 900°C.

**[0093]** Moreover, in the Ni-based super alloys according to Examples 1 to 15, the content of Co is particularly limited to less than 0.10%. Therefore, they are not only excellent in grindability but also inexpensive in material costs.

**[0094]** Therefore, in the case where these Ni-based super alloys are used as materials for engine valves, it may be easy to improve engine performance. Furthermore, the life of grindstone to be used at grinding of products is lengthened and also surface processing accuracy of the products can be improved.

**[0095]** While Ni-based super alloys of the present invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof

**[0096]** The present application is based on Japanese Patent Application No. 2006-079447 filed on March 22, 2006, and the contents thereof are incorporated herein by reference.

#### 25 Claims

20

45

1. A Ni-based super alloy comprising, by mass %:

C: 0.01 to 0.15 %: 30 Si: 1 % or less; Mn: 1 % or less; P: 0.02 % or less; S: 0.01 % or less; Co: less than 0.10 %; 35 Cr: 16 to 22 %; Mo: 4 to 10 %; W: 5 % or less; AI: 1.2 to 2.5 %; Ti: 2.4 to 4 %: 40 B: 0.001 to 0.05 %; Zr: 0.01 to 0.5 %; Fe: 1 % or less; and

a balance of Ni and inevitable impurities.

- The Ni-based super alloy according to claim 1, wherein Mo + 1/2W is 4 to 10 %.
- **3.** The Ni-based super alloy according to claim 1 or 2, which further comprises at least one selected from the groups consisting of:

Nb: 0.1 to 3 %; and Ta: 0.1 to 3 %.

55 **4.** The Ni-based super alloy according to any one of claims 1 to 3, which further comprises at least one selected from the group consisting of:

Ca: 0.001 to 0.03 %;

Mg: 0.001 to 0.03 %; and

55

REM: 0.001 to 0.1 %. **5.** The Ni-based super alloy according to any one of claims 1 to 4, which further comprises: 5 Cu: 0.01 to 2 %. 6. The Ni-based super alloy according to any one of claims 1 or 5, which further comprises: V: 0.05 to 1 %. 10 7. The Ni-based super alloy, in particular according to any one of claims 1 to 6, which is relatively inexpensive, excellent in high-temperature mechanical properties, and excellent in grindability. 15 20 25 30 35 40 45 50



## **EUROPEAN SEARCH REPORT**

Application Number EP 07 00 5969

	DOCUMEN IS CONSIDE	RED TO BE RELEVANT		
Category	Citation of document with inc of relevant passa		Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 1 338 663 A1 (SUN 27 August 2003 (2003 * page 3, lines 14-3		1-7	INV. C22C19/05
Х	EP 1 340 825 A (DAII 3 September 2003 (20 * paragraphs [0002] [0025]; example 7;	, [0008], [0024],	1-7	
P,X	EP 1 696 108 A (DAII HONDA MOTOR CO LTD 30 August 2006 (2006 * paragraphs [0001]	5-08-30)	1-7	
А	US 2002/195175 A1 (; AL) 26 December 2002 * paragraphs [0003] [0043] - [0058] *		1-7	
А	EP 0 889 207 A1 (DA: DAIDO STEEL COMPANY 7 January 1999 (1999 * page 3, lines 16-	9-01-07)	1-7	TECHNICAL FIELDS SEARCHED (IPC)
Α	US 4 871 512 A (TAK/ AL) 3 October 1989 * column 1, lines 58	AGI YOSHIAKI [JP] ET (1989-10-03) 3-66 * 	1-7	
	The present search report has be	een drawn up for all claims		
	Place of search	Date of completion of the search	Do.	Examiner
	Munich	2 July 2007		lle, Susett
X : part Y : part docu A : tech O : non	ATEGORY OF CITED DOCUMENTS icularly relevant if taken alone icularly relevant if combined with another interest of the same category nological background written disclosure rediate document	T : theory or principle E : earlier patent doc after the filing date er D : document cited in L : document cited fo	ument, but publi e n the application or other reasons	ished on, or

## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 07 00 5969

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

02-07-2007

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 1338663	A1	27-08-2003	CA WO US	2396578 / 0240728 / 2003005981 /	A1 23-05-200
EP 1340825	Α	03-09-2003	JP US	2003253363 / 2003164213 /	
EP 1696108	Α	30-08-2006	JP US	2006225756 / 2006157171 /	
US 2002195175	A1	26-12-2002	JР	2002363674	A 18-12-200
EP 0889207	A1	07-01-1999	AT DE DE JP US	69810197 I	T2 09-10-200 A 26-01-199
US 4871512	A	03-10-1989	CA DE GB JP JP JP	1255927 / 3540287 / 2167440 / 1488534 ( 61119640 / 63039654	A1 22-05-198 A 29-05-198 C 23-03-198 A 06-06-198

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

## REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

## Patent documents cited in the description

- JP 61119640 A [0003]
- JP 5059472 A [0004]

• JP 2006079447 A [0096]