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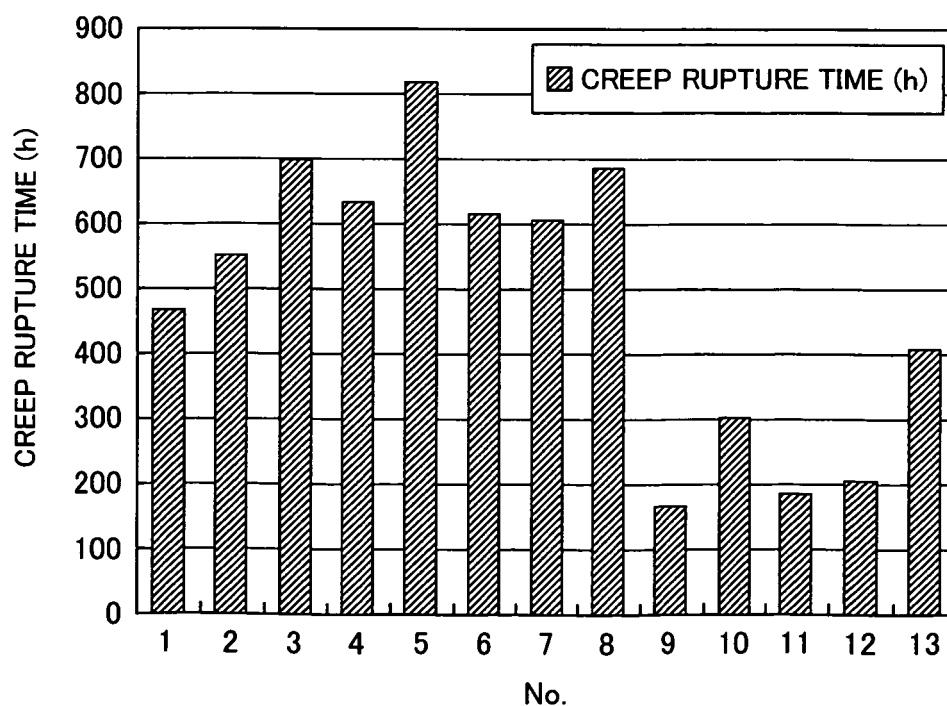
BA ME RS(30) Priority: **04.09.2009 JP 2009204246**(71) Applicant: **Hitachi, Ltd.****Chiyoda-ku****Tokyo 100-8280 (JP)**

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• **Sato, Jun****Tokyo 100-8220 (JP)**• **Imano, Shinya****Tokyo 100-8220 (JP)**• **Doi, Hiroyuki****Tokyo 100-8220 (JP)**(74) Representative: **Beetz & Partner****Patentanwälte****Steinsdorfstrasse 10****80538 München (DE)**(54) **Ni based casting alloy and turbine casing**

(57) A Ni based cast alloy consisting essentially of
 C: 0.01 to 0.2 % by weight, Si: 0.5 to 4.0 % by weight,
 Cr: 14 to 22 % by weight, Mo + W: 4.0 to 10 % by weight,
 B: 0.001 to 0.02 % by weight, Co: up to 10 % by weight,

Al: up to 0.5 % by weight, Ti: up to 0.5 % by weight, Nb:
 up to 5.0 % by weight, Fe: up to 10 % by weight, the
 balance being Ni and incidental impurities, wherein a γ'
 phase precipitates in a matrix phase thereof.

FIG. 2**EP 2 292 807 A1**

Description

FIELD OF THE INVENTION:

5 **[0001]** The present invention relates to a Ni based casting alloy suitable for high temperature parts for steam turbines and a steam turbine casing.

BACKGROUND OF THE INVENTION:

10 **[0002]** In order to increase a power generation efficiency of a steam turbine, an increase in temperature of steam is necessary. As for materials that withstand high temperatures and high pressures, ferritic steels such as Cr-Mo-V steels or 12Cr steels have been utilized. The ferritic steels are excellent in high temperature strength and productivity and they are of low cost. Therefore, they have been utilized as forging materials for turbine rotors and casting materials for turbine casings, etc. (Patent document Nos. 1, 2).

15 **[0003]** Ni based superalloys that have higher strength than the conventional ferritic heat resisting steels have been utilized as high temperature parts for gas turbines. The Ni based superalloys have higher heat resisting temperature than the ferritic heat resisting steels, and when they are utilized, it is expected to obtain higher power generation efficiency.

[0004] The Ni based superalloys generally contain Al and/or Ti, which precipitates an intermetallic compound phase of $\text{Ni}_3(\text{Al,Ti})$ type, called γ' phase to thereby increase a mechanical strength (patent document No. 3 etc). Since the γ' phase increases mechanical strength as temperatures increase, it is suitable for strengthening phase for heat resisting materials. However, these elements have a problem in production of the steel because they tend to be oxidized during melting of the materials for the steels. If Al and Ti are oxidized, a desired mechanical strength is not obtained because of shortage of strengthening elements in the alloys, and in addition, reliability of the alloys decrease because of inclusion of the oxides as casting defects in the alloys. Therefore, in a melting process for the Ni based superalloys, such high technical melting process as electroslog re-melting or vacuum arc re-melting have been essential (patent document No. 4). The patent document No. 4 relates to a Ni-Fe based alloy containing Al and Ti. However, the above technologies cannot be applied to such large scale and complicated parts such as turbine casings, and therefore, it was difficult to produce Ni based casting alloys of high temperature parts with high mechanical strength and high reliability.

25 **[0005]** If, in conventional Ni based alloys containing Cr, Mo + W and B, Al and/or Ti is not added in order to avoid oxidation, a sufficient mechanical strength is not obtained because the γ' phase for strengthening by precipitation does not exist. Therefore, it is impossible to elevate temperatures of steam to obtain high power generation efficiency.

PRIOR ART:

35 **[0006]**

Patent document No. 1: Japanese patent laid-open 2006-22343

Patent document No. 2: Japanese patent laid-open 2007-92123

Patent document No. 3: Japanese patent laid-open 2000-169924

40 Patent document No. 4: Japanese patent laid-open 2006-118016

SUMMARY OF THE INVENTION:

45 **[0007]** It is an object of the present invention to provide Ni based cast alloys having the precipitated γ' phase and high mechanical strength, which can be produced by a low cost casting process that is similar to that of the conventional heat resisting steels.

[0008] According to one aspect of the Ni based casting alloy of the present invention, the Ni based cast alloy has an as-cast structure and consists essentially of C: 0.01 to 0.2 % by weight, Si: 0.5 to 4.0 % by weight, Cr: 14 to 22 % by weight, Mo + W: 4.0 to 10 % by weight, B: 0.001 to 0.02 % by weight, Co: up to 10 % by weight, Al: up to 0.5 % by weight, Ti: up to 0.5 % by weight, Nb: up to 5.0 % by weight, Fe: up to 10 % by weight, the balance being Ni and incidental impurities, wherein γ' phase precipitates in a matrix phase. The matrix phase in this specification means a dominant part of an alloy structure, and the alloy structure of the alloy means a group of different phases and grains constituting the alloy.

50 **[0009]** According to one aspect of the present invention, the cast alloy consisting essentially of C: 0.01 to 0.2 % by weight, Si: 0.5 to 4.0 % by weight, Cr: 14 to 22 % by weight, Mo + W: 4.0 to 10 % by weight, B: 0.001 to 0.02 % by weight, the balance being Ni and incidental impurities.

[0010] According to another aspect of the present invention, the cast alloy consists essentially of C: 0.01 to 0.2 % by weight, Si: 0.5 to 4.0 % by weight, Cr: 14 to 22 % by weight, Co: 0.1 to 10 % by weight, Al: 0.1 to 0.5 % by weight, Ti:

0.1 to 0.5 % by weight, Nb: 1.0 to 4.0 % by weight, Mo + W: 4.0 to 10 % by weight, Fe: 0.1 to 10 % by weight, B: 0.001 to 0.02 % by weight, the balance being Ni and incidental impurities.

[0011] According to still another aspect of the present invention, the Ni based cast alloy consists essentially of C: 0.05 to 0.15 % by weight, Si: 1.0 to 3.5 % by weight, Cr: 15 to 20 % by weight, Al: 0.1 to 0.5 % by weight, Ti: 0.1 to 0.5 % by weight, Nb: 1.0 to 4.0 % by weight, Co: 1.0 to 5 % by weight, Fe: 1.0 to 5 % by weight, Mo + W: 5.0 to 8 % by weight, B: 0.002 to 0.01 % by weight, the balance being Ni and incidental impurities.

[0012] These alloys precipitate the γ' Ni_3Si phase as the strengthening phase by a suitable heat treatment, and the phase can exist during in its service, to thereby obtain excellent high temperature mechanical strength. Since there is no loss of strengthening elements by oxidation even in conventional melting process and no inclusion of oxides, reliability of the castings is high, which are suitable for high temperature parts such as steam turbine casings.

[0013] According to the above alloy compositions, it is possible to provide high mechanical strength Ni based casting alloys, which can be produced by low cost conventional melting process. In addition, it is possible to produce steam turbine casting parts with high reliability.

BRIEF DESCRIPTION OF THE DRAWINGS:

[0014]

Fig. 1 is a diagrammatic view of the alloy structure of the present invention.

Fig. 2 is a graph showing creep rupture time of the alloys of the examples.

Fig. 3 a graph showing creep rupture elongation of the alloys of the examples.

Fig. 4 shows a cross sectional view of a steam valve for a steam turbine to which the present invention is applied.

Fig. 5 shows a cross sectional view of a steam turbine rotor to which the present invention is applied.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS:

[0015] The present inventors have investigated influences of alloying elements on properties of Ni based alloys, and as a result, they invented Ni based casting alloys suitable for steam turbines. In the following, alloying elements and adding ranges thereof are explained.

(1) C: Carbon solid-dissolves into a matrix phase to increase a tensile strength at high temperatures, and forms carbides such as MC, M_{23}C_6 to strengthen grain boundaries. These effects becomes when 0.01 % by weight of carbon is contained. If the amount exceeds 0.2 % by weight, coarse eutectic carbides precipitate to lower ductility of the alloys. Thus, 0.2 % by weight is an upper limit. An amount of 0.05 to 0.15 % by weight is a preferable range.

(2) Si: Si has been known as an effective element for deoxidizing and casting performance. In the present invention, silicon is added as a strengthening element. An excess amount of silicon lowers a melting point, and forms undesirable phase. In the present invention, after detailed investigations of influences of elements, it is possible to add a larger amount of silicon than the conventional alloys by balancing the elements. In order to precipitate Ni_3Si as the strengthening phase, 0.5 % by weight of silicon is necessary, but if the amount exceeds 4 % by weight, segregation at solidification becomes large to thereby lower strength at grain boundaries. A preferable amount range is 1.0 to 3.5 % by weight.

(3) Cr: Chromium increases anti-oxidation property and high temperature anti-corrosion property by forming dense oxide film made of Cr_2O_3 on the surface of the alloy. At least 14 % by weight of Cr is necessary for the high temperature parts. If the amount exceeds 22 % by weight, a σ phase precipitates to decrease ductility and rupture ductility. A preferable range is 15 to 20 % by weight.

(4) Mo, W: Molybdenum and tungsten strengthen the matrix phase by solid-solution strengthening. In order to obtain sufficient strengthening, a total amount of them should be 4 % by weight or more, but if the total amount exceeds 10 % by weight, the elements may accelerate formation of hard and brittle intermetallic compound phase and may deteriorate ductility at high temperatures. A preferable total amount range is 6 to 9 % by weight.

(5) B: A small amount of boron strengthens grain boundaries and improves creep strength. An excess amount of B precipitates undesirable phases and lowers melting point, which may be a cause of partial melting. An amount of B should be 0.001 to 0.02 % by weight. A preferable range is 0.001 to 0.02 % by weight.

(6) Co: Cobalt improves high temperature strength by solid-dissolving into the matrix phase to thereby substitute with Ni and contributes to improvement of high temperature anti-corrosion property. In the alloy composition of the present invention, 0.1 % by weight or more is necessary for the above properties. An excess amount assists precipitation of undesirable phases such as the σ phase or μ phase, and an upper limit is 10 % by weight.

(7) Al: In conventional Ni based alloys, Al has been added to form Ni_3Al phase as a strengthening element. In the present invention, Al contributes to strengthening of the Ni_3Si phase. However, since Al is an active element, Al is

heavily oxidized during casing in air to deteriorate reliability of the products. An upper limit of Al is 0.5 % by weight, accordingly. A preferable range is 0.1 to 0.4 % by weight.

(8) Ti: Titanium, similarly to Al, stabilizes and strengthens the γ' phase. Since Ti is also an active element, an upper limit is 0.5 % by weight. A preferable range is 0.1 to 0.4 % by weight.

(9) Nb: Niobium contributes to strengthening of the γ' phase, similarly to Al and Ti. Since Nb is less oxidative than Al and Ti, 5 % by weight as an upper limit is acceptable. If an excess amount is added, Ni_3Nb is formed to deteriorate stability of the alloy structure for a long time.

(10) Fe: Iron contributes to solid-solution strengthening by substituting with Ni. From the view point of economy, it is preferable to add iron as much as possible, but Fe is relatively poor in stabilizing the γ' phase, compared with Ni. Thus, an upper limit is 10 % by weight. A preferable range is 1.0 to 5.00 % by weight.

[0016] Table 1 shows alloy compositions of the example Nos. 1 to 8 and comparative example alloy Nos. 1 to 5.

[0017] 10 Kgs of each of the alloys was melted in air, and the molten metal was casted in a sand mold to produce a columnar cast ingots with a diameter of 100 mm. The resulting ingots were subjected to heat treatment at 1150 °C for 30 minutes, and 720 °C for 24 hours. Thereafter, alloy structures of the ingots were observed, and the ingots were subjected to high temperature creep tests.

[0018] Among the heat treatments, the first one was a solution heat treatment, which makes non-uniform cast structure uniform. The higher the temperature, the better the result is obtained; however, in order to avoid partial melting or coarsening of the structure, the heat treatment at 1100 to 1200 °C is preferable. A heat treatment after the solution heat treatment is carried out for precipitating a strengthening phase. Though a temperature for the second heat treatment may be chosen based on materials or use conditions of components, an amount of precipitation of the strengthening phase is too small if the temperature is higher than 800 °C, but on the other hand, precipitation is hard to take place if the temperature is lower than 700 °C. Therefore, the temperature for precipitating the strengthening phase is preferably 700 to 800 °C.

Table 1

No.	Alloy	Alloying elements											
		Ni	C	Si	Cr	Mo	W	B	Co	Al	Ti	Nb	Fe
1	Ex. 1	Bal.	0.05	1.6	18.0	2.0	4.0	0.005	-	-	-	-	-
2	Ex. 2	Bal.	0.04	2.7	16.0	4.0	2.5	0.005	-	-	-	-	-
3	Ex. 3	Bal.	0.05	3.6	16.0	-	5.0	0.004	-	-	-	-	-
4	Ex. 4	Bal.	0.05	3.0	18.0	8.0	-	0.004	2.0	0.2	0.2	-	2.5
5	Ex. 5	Bal.	0.05	3.0	18.0	5.0	2.5	0.004	2.0	0.2	0.2	3.0	2.5
6	Ex. 6	Bal.	0.05	2.5	20.0	5.0	2.5	0.004	-	0.2	0.1	5.0	5.0
7	Ex. 7	Bal.	0.1	1.6	18.0	5.0	-	0.002	5.0	0.4	-	4.0	5.0
8	Ex. 8	Bal.	0.1	3.0	20.0	3.0	3.0	0.002	8.0	-	0.2	-	5.0
9	Com. Ex. 1	Bal.	0.05	0.5	18.0	8.0	-	0.004	5.0	-	-	-	-
10	Com. Ex. 1	Bal.	0.05	4.5	20.0	8.0	-	0.004	-	-	-	5.0	10.0
11	Com. Ex. 1	Bal.	0.05	2.5	16.0	2.0	4.0	0.004	10.0	0.5	2.0	4.0	2.0
12	Com. Ex. 1	Bal.	0.05	2.5	18.0	8.0	-	0.004	2.0	1.5	-	2.0	-
13	Com. Ex. 1	Bal.	0.05	0.1	22.0	9.0	-	0.004	0.5	0.2	0.2	4.0	2.5

[0019] Fig. 1 shows a diagrammatic view of the alloy structures of example alloy Nos. 1 to 8. In the inventive alloys, the γ' phase for strengthening precipitates dispersedly and a small amount of carbides precipitate at grain boundaries. The structure is similar to the conventional γ' precipitation strengthening type Ni based alloys. This shows an effect of Si addition.

[0020] On the other hand, in comparative example alloy No. 1, since an amount of Si is small, and since no Al and T are added, the γ' phase did not precipitate. In the comparative alloy No. 2, since a sufficient amount of Si was added, the γ' phase precipitated, but large precipitation of the γ' phase was observed at the grain boundaries and boundaries of dendrites. In comparative alloy No. 3, though Al and Ti were added in addition to Si, it was observed that oxides

formed during casting were included in the alloy. The comparative alloy No. 4 is the same. The comparative example alloy No. 5 corresponds to alloy 625, which has been commercially available on the market. Though inclusion of oxides was not observed since amounts of Al and Ti were small, alloy materials that have been subjected to holding at high temperatures such as creep tests, precipitation of Ni_3Nb was observed.

[0021] Kinds of precipitates and evaluation results of soundness of the alloy structures are shown in Table 2.

Table 2

No.	Alloy	Alloy Structure	Soundness of structure	Creep rupture time (h)	Creep Rupture elongation (%)
1	Ex. 1	γ' and carbides	○	468	35
2	Ex. 2	γ' and carbides	○	553	33
3	Ex. 3	γ' and carbides	○	701	25
4	Ex. 4	γ' and carbides	○	635	27
5	Ex. 5	γ' and carbides	○	820	26
6	Ex. 6	γ' and carbides	○	612	32
7	Ex. 7	γ' and carbides	○	605	32
8	Ex. 8	γ' and carbides	○	688	31
9	Com. Ex. 1	-	△	165	41
10	Com. Ex. 2	γ' and carbides	△	305	10
11	Com. Ex. 3	γ' and carbides, oxides	×	184	8
12	Com. Ex. 4	γ' and carbides, oxides	×	206	7
13	Com. Ex. 5	γ' and carbides, Ni_3Nb phase	△	410	27

[0022] Figs. 2 and 3 show creep rupture time and creep rupture elongation of the alloys shown in Table 1. The creep test was conducted at 700 °C under a load of 333 MPa. Every inventive alloy exhibited superior creep rupture time to the conventional alloy (Comparative example alloy No. 5). Addition of Si precipitated the γ' phase to thereby improve high temperature strength. As to the high temperature ductility, 25 % or more of elongation was observed.

[0023] The comparative example alloy No. 1 contained small amounts of strengthening elements and no γ' phase exists. Therefore, it has low creep rupture strength. In the comparative example alloy No. 2, which contained a large amount of Si, it has higher creep rupture strength than that of the comparative example alloy No. 1, but it has a low creep elongation. This is because large precipitates existed at grain boundaries and dendrite boundaries, which means the amount of Si was excess.

[0024] In the comparative example alloy Nos. 3 and 4, there was observed inclusion of oxides. Rupture cracks were found wherein the ruptures started at included oxides so that the creep rupture time and creep rupture elongation were quite low. Accordingly, active amounts of Al and Ti should be made small to improve characteristics of the alloys for the present invention. Since the amounts of Al and Ti in the comparative alloy No. 5 are controlled to small amounts, deterioration of characteristics due to oxidation was not observed, but Ni_3Nb precipitated as the time goes at high temperatures. Therefore, the example alloy of the present invention showed excellent structure stability by virtue of Si.

[0025] The alloys of the present invention are applied to high temperature components such as a casing for a rotor or a steam valve of a steam turbine.

[0026] Fig. 4 shows a cross sectional view of a steam valve comprising a valve casing 1, a valve body 2, a valve sheet 3, a piping 4, a sleeve 5, a shaft bush 6 and a valve shaft 7. The alloy of the present invention is applied to the valve casing 1, valve body 2 and valve sheet 3, which are produced by casting. These components that have as-cast structures having γ' precipitate in the matrix phase are subjected to proper heat treatments before assembling. Detailed descriptions of the steam valve are omitted because the structure and functions of the components are well known in the art.

[0027] Fig. 5 shows a cross sectional view of a steam turbine rotor comprising nozzles 14, 15, blades 16, 17, inner casings 18, 20, 21, outer casings 19, 22, flange and elbow 25, a steam inlet 28, a rotor shaft 33, a nozzle box 38 and a journal 43. The alloy of the present invention is applied to the inner casings 18, 20, 21 and the outer casings 19, 22,

which are produced by casting. These components as-cast structures having γ' precipitate in the matrix phase are subjected to proper heat treatments before assembling. Detailed descriptions of the steam turbine rotor are omitted because the structure and functions of the components are well known in the art.

Claims

1. A Ni based cast alloy having an as-cast structure and consisting essentially of C: 0.01 to 0.2 % by weight, Si: 0.5 to 4.0 % by weight, Cr: 14 to 22 % by weight, Mo + W: 4.0 to 10 % by weight, B: 0.001 to 0.02 % by weight, Co: up to 10 % by weight, Al: up to 0.5 % by weight, Ti: up to 0.5 % by weight, Nb: up to 5.0 % by weight, Fe: up to 10 % by weight, the balance being Ni and incidental impurities, wherein a γ' phase precipitates in a matrix phase thereof.
2. A Ni based cast alloy having an as-cast structure and consisting essentially of C: 0.01 to 0.2 % by weight, Si: 0.5 to 4.0 % by weight, Cr: 14 to 22 % by weight, Mo + W: 4.0 to 10 % by weight, B: 0.001 to 0.02 % by weight, the balance being Ni and incidental impurities, wherein a γ' phase precipitates in a matrix phase thereof.
3. A Ni based cast alloy having an as-cast structure and consisting essentially of C: 0.01 to 0.2 % by weight, Si: 0.5 to 4.0 % by weight, Cr: 14 to 22 % by weight, Co: 0.1 to 10 % by weight, Al: 0.1 to 0.5 % by weight, Ti: 0.1 to 0.5 % by weight, Nb: 1.0 to 4.0 % by weight, Mo + W: 4.0 to 10 % by weight, Fe: 0.1 to 10 % by weight, B: 0.001 to 0.02 % by weight, the balance being Ni and incidental impurities, wherein a γ' phase precipitates in a matrix phase thereof.
4. A Ni based cast alloy having an as-cast structure and consisting essentially of C: 0.05 to 0.15 % by weight, Si: 1.0 to 3.5 % by weight, Cr: 15 to 20 % by weight, Al: 0.1 to 0.5 % by weight, Ti: 0.1 to 0.5 % by weight, Nb: 1.0 to 4.0 % by weight, Co: 1.0 to 5 % by weight, Fe: 1.0 to 5 % by weight, Mo + W: 5.0 to 8 % by weight, B: 0.002 to 0.01 % by weight, the balance being Ni and incidental impurities, wherein a γ' phase precipitates in a matrix phase thereof.
5. The Ni based cast alloy according to claim 1, wherein a γ' phase precipitates in a matrix phase thereof.
6. The Ni based cast alloy according to claim 2, wherein a γ' phase precipitates in a matrix phase thereof.
7. The Ni based cast alloy according to claim 3, wherein a γ' phase precipitates in a matrix phase thereof.
8. The Ni based cast alloy according to claim 1, the alloy having been subjected to heat treatment at 700 to 800 °C to precipitate Ni_3Si type intermetallic compound.
9. The Ni based cast alloy according to claim 1, the alloy having been prepared by melting and casting in air or inert gas atmosphere.
10. A high temperature part for a steam turbine made of the alloy according to claim 1.
11. A high temperature part for a steam turbine made of the cast alloy according to claim 2.
12. A high temperature part for a steam turbine made of the alloy according to claim 3.
13. A steam turbine casing made of cast alloy according to claim 1.
14. A steam turbine casing made of cast alloy according to claim 2.
15. A steam turbine casing made of cast alloy according to claim 3.

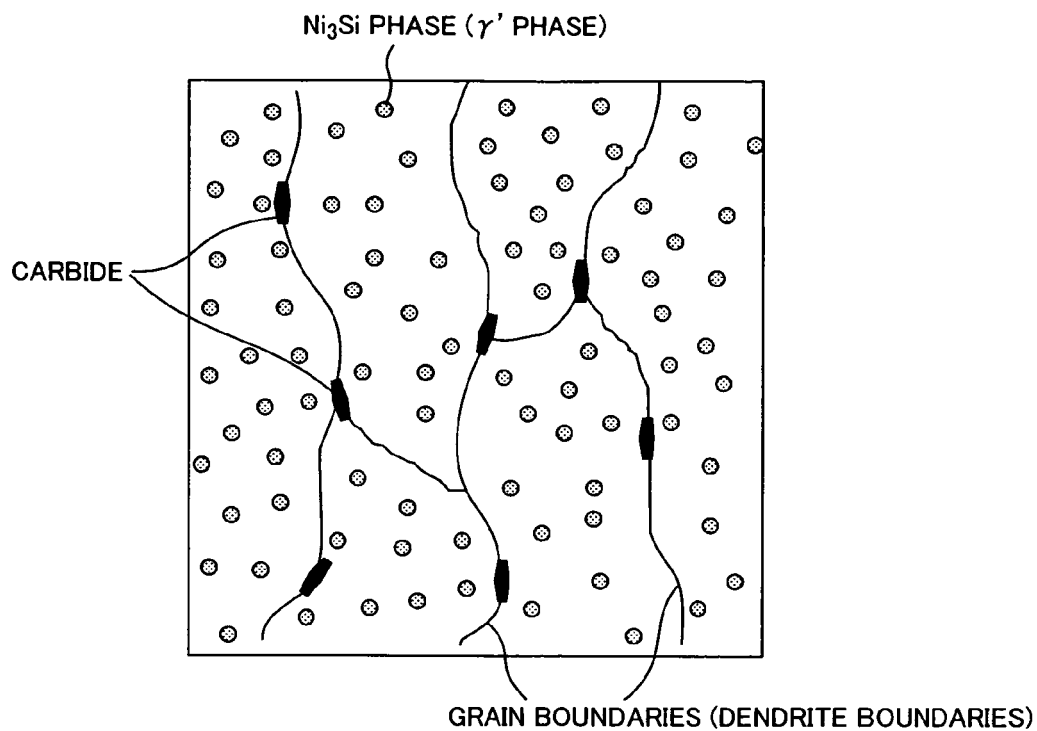
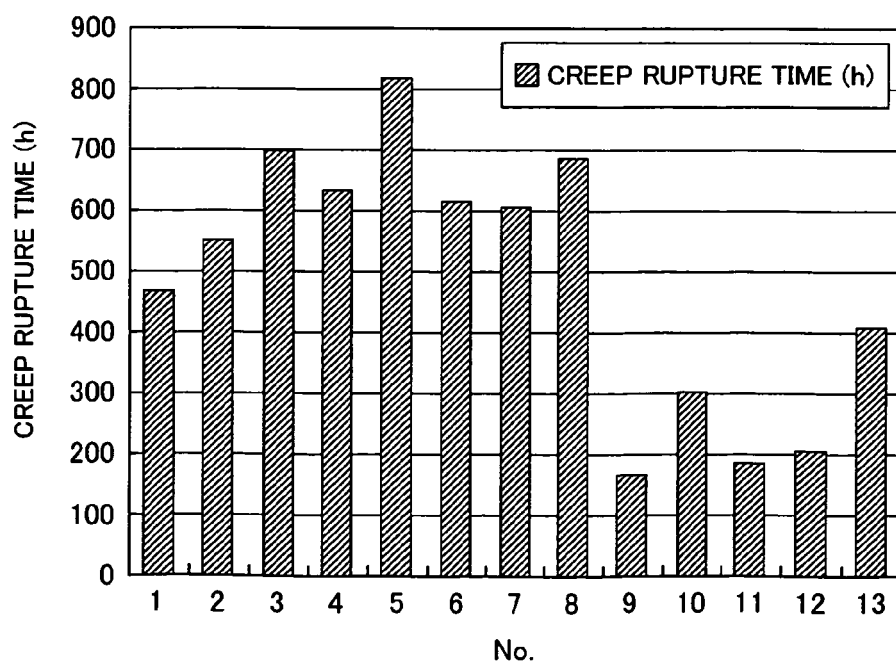
FIG. 1**FIG. 2**

FIG. 3

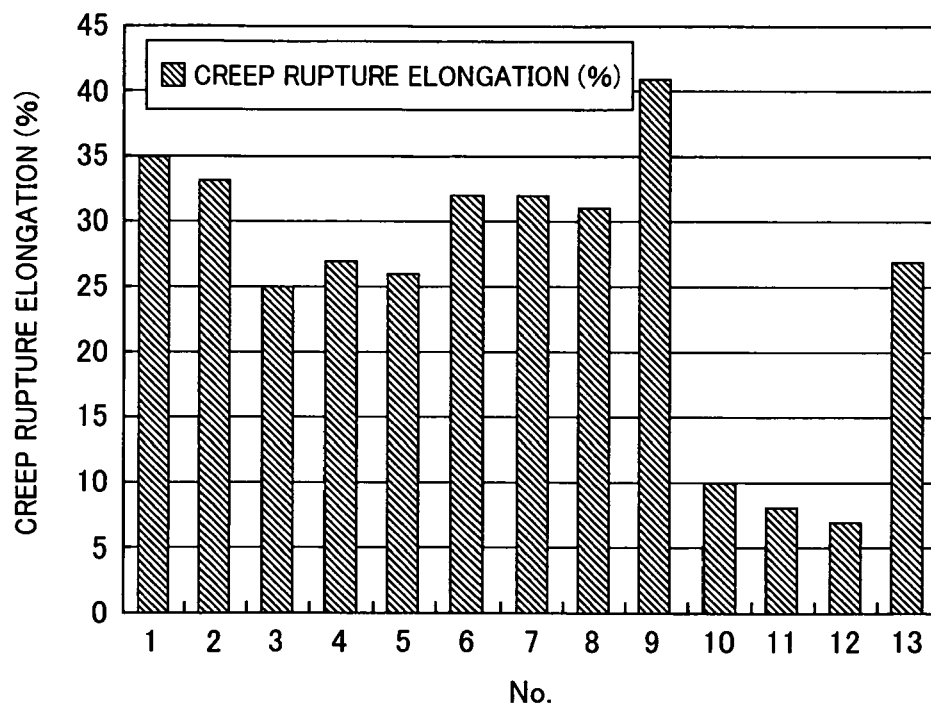


FIG. 4

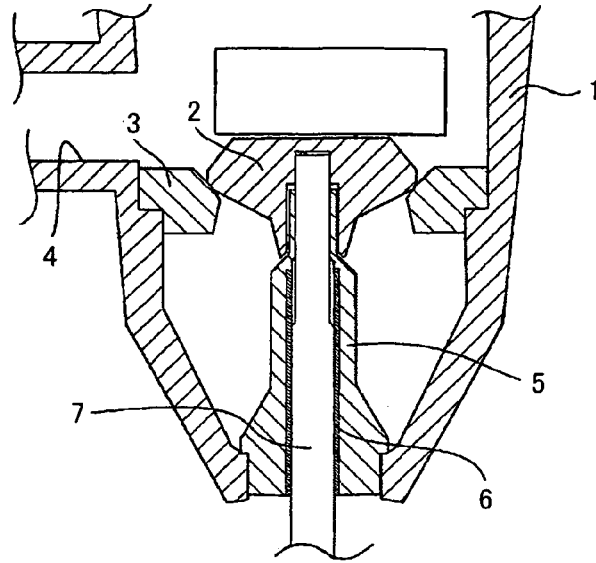
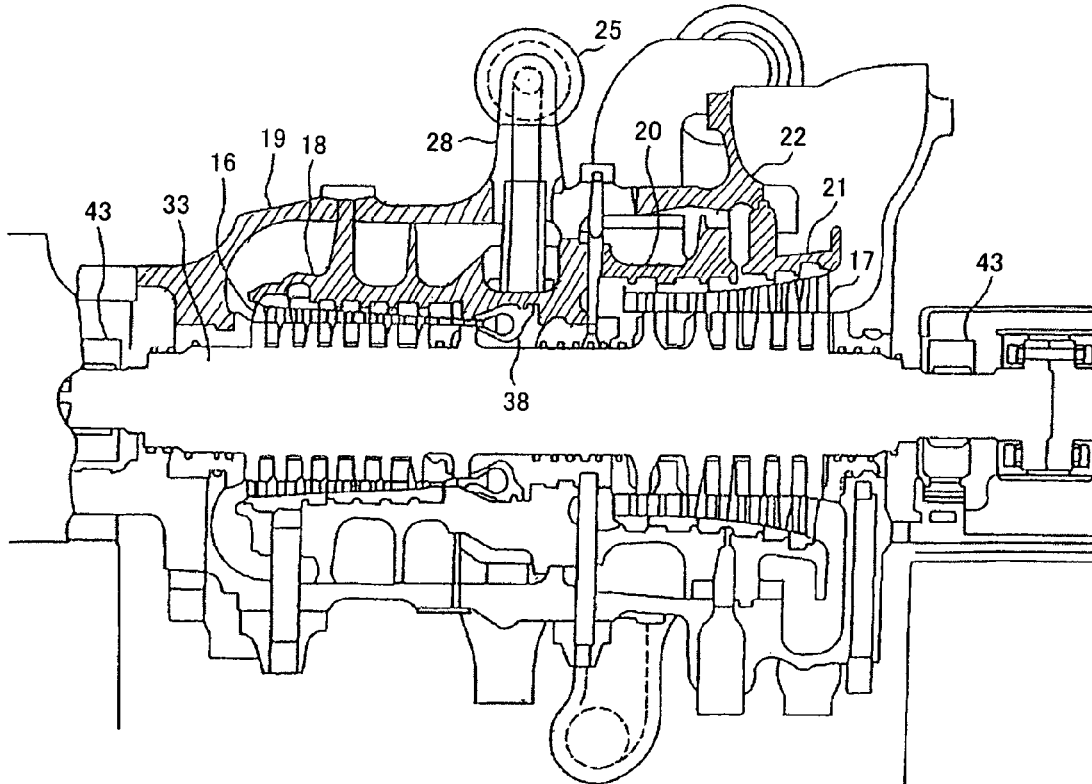


FIG. 5





EUROPEAN SEARCH REPORT

Application Number
EP 10 00 8945

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
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EP 10 00 8945

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
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