(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 795 621 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
13.06.2007 Bulletin 2007/24

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

(21) Application number: **06025253.3**

(22) Date of filing: **06.12.2006**

(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 NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK YU

(30) Priority: **09.12.2005 JP 2005356445**

(71) Applicant: **Hitachi, Ltd.**
Chiyoda-ku
Tokyo (JP)

(72) Inventors:
- **Tamaki, Hideki, Hitachi, Ltd., Int. Property Group**
  Chiyoda-ku
  Tokyo 100-8220 (JP)
- **Yoshinari, Akira, Hitachi, Ltd., Int. Prop. Group**
  Chiyoda-ku
  Tokyo 100-8220 (JP)
- **Okayama, Akira, Hitachi, Ltd., Int. Prop. Group**
  Chiyoda-ku
  Tokyo 100-8220 (JP)
- **Doi, Hiroyuki, Hitachi, Ltd., Int. Prop. Group**
  Chiyoda-ku
  Tokyo 100-8220 (JP)

(74) Representative: **Beetz & Partner**
Patentanwälte,
Steinsdorfstrasse 10
80538 München (DE)

(54) High-strength and high-ductility ni-base superalloys, parts using them, and method of producing the same

(57) This invention provides an Ni-base superalloy capable of providing the castings with high high-temperature strength and excellent ductility no matter whether it is used for the directionally solidified castings or conventional castings, and suited for casting of the centrifugal wheels of industrial gas turbines, turbo chargers or microturbines. This Ni-base superalloy contains, in percent by weight, 0.06 to 0.3% of C, 0.01 to 0.05% of B, 0.5 to 3.0% of Hf, 10.2 to 25% of Co, 1 to 12% of Ta, 1.5 to 16% of Cr, 2 to 15% of W, 3.5 to 6.5% of Al, 0.5 to 9% of Re, and 0.2 to 2% of Nb.

Printed by Jouve, 75001 PARIS (FR)

Description

Field of the Invention

[0001] The present invention relates to Ni-base superalloys having excellent high-temperature strength and ductility, more particularly to the Ni-base superalloys showing high strength and excellent ductility no matter whether they are used for conventional castings or directionally solidified castings. The present invention also pertains to a centrifugal wheel for turbo chargers or microturbines or a rotating blade or a stationary vane for axial flow gas turbines, which have been produced by casting the said Ni-base superalloys.

Background of the Invention

[0002] The Ni-base supperalloys are used for the parts exposed to high temperatures, such as a rotating blade or a stationary vane, in the gas turbines for aeroengines or the industrial gas turbines. Such Ni-base superalloys are also used for the centrifugal wheels for turbo chargers or microturbines.

[0003] The combustion gas temperature in the gas turbines has a tendency to rise up constantly for the improvement of thermal efficiency, and in coordination with this, directionally solidified alloy castings have come to be used in place of the conventional castings for the rotating blade and the stationary vane. Also, in the gas turbines for aeroengines which are relatively small in size, the single crystal blades with excellent high-temperature strength have come in practice.

[0004] Among the Ni-base superalloys developed for the directionally solidified castings, those containing Ti as a strengthening element are dominant. (See, for instance, Patent Document 1.)

[0005] Most of the alloys developed for the single crystal castings contain no grain boundary strengthening element, so that they are hardly applicable to the large-sized parts, such as industrial gas turbines, which tend to form grain boundaries during casting thereof. In order to allow application of the single crystal castings to the large-sized parts, there have been developed the alloys in which a grain boundary strengthening element such as C, B. Hf or Zr has been incorporated. (See, for instance, Patent Document 2.) However, the industrial gas turbine blades are large in size and their internal cooling mechanism is complicate, so that grain boundaries tend to form during casting, and further the yield of the single crystal blades is by far lower than that of the gas turbine blades for aeroengines. Thus, development of a high-strength Ni-base superalloy for directionally solidified castings has been craved.

[0006] On the other hand, conventional castings are used for the centrifugal wheels of turbo chargers or microturbines which have difficulties in being directionally solidified in the direction parallel to the centrifugal stress. (See, for instance, Patent Document 3.) This is because the conventional castings produced from a high-strength Ni-base superalloy developed with directional solidification as a premise are extremely low in ductility due to low grain boundary strength and can not be applied to the centrifugal wheels.

Patent Document 1: USP 5,069,873
Patent Document 2: USP 6,051,083
Patent Document 3: USP 3,720,509

Brief Summary of the Invention

[0007] The alloys developed for the single crystal castings, although containing a grain boundary strengthening element, are low in strength at the time of formation of grain boundaries in contrast with very high intergranular strength, and can be therefore hardly applied to the large-sized blades of intricate configuration which tend to cause formation of grain boundaries during casting.

[0008] In the case of the alloys developed for the directionally solidified castings, it is possible to improve strength in the direction of solidification by increasing the volume ratio of γ' phase, which is a precipitation strengthening phase, and the amount of incorporation of a refractory metal element such as W, Re or Ta, but on the other hand the grain boundary strength is relatively lowered. The alloys enhanced in strength in the solidification direction have the problem that they are remarkably lowered in strength in the direction perpendicular to the direction of solidification, that is, in grain boundary strength.

[0009] The alloys disclosed in Patent Document 2, although having a sufficient grain boundary strength to improve the single crystal blade casting yield, are rather unsatisfactory in grain boundary strength for application to the directionally solidified blades for industrial gas turbines which are large in size and intricate in configuration. The alloys for directionally solidified castings disclosed in Patent Document 1, although substantially satisfactory in grain boundary strength, are low in strength in the solidified direction.

[0010] The alloys for conventional castings shown in Patent Document 3, although having a moderate ductility, are low in high-temperature strength and required to be improved high-temperature strength for application to the centrifugal wheels of turbo chargers or microturbines.

[0011] An object of the present invention is to provide Ni-base superalloys which are capable of providing a high high-temperature strength and an excellent ductility no matter whether they are used for directionally solidified castings or conventional castings, and which find their particular useful application to the centrifugal wheels for industrial gas turbines, turbo charges or microturbines.

[0012] In an embodiment of the present invention, there is provided an Ni-base superalloy comprising, in percent (%) by weight, 0.06 to 0.3% of C, 0.01 to 0.05% of B, 0.2 to 3.0% of Hf, 10.2 to 25% of Co, 1 to 12% of Ta, 1.5 to 16% of Cr, 0 to 0.95% of Mo, 2 to 15% of W, 3.5 to 6.5% of Al, 0.5 to 9% of Re, 0.2 to 2% of Nb, 0 to 1% of V, 0 to 0.02% of Zr, 0 to 2% of at least one element selected from the platinum group elements, 0 to 2% of at least one element selected from the rare earth elements, 0 to 0.1% of at least one element selected from the alkaline earth metals and Si, 0 to 5% of at least one element selected from Fe, Ga and Ge, and the balance consisting of Ni and unavoidable impurities. This alloy shows high high-temperature strength and excellent ductility no matter whether it is used for directionally solidified or conventional castings. The "unavoidable impurities" refer to the impurities or contaminants which get mixed in the alloys in company with the elemental materials when they are added, for instance impurities contained in Cr material. Examples of such impurities are Si, S, O, N, P, Mn and Cu.

[0013] The Ni-base superalloy having the said composition shows high high-temperature strength when used for single crystal castings. When Hf is contained in an amount of 1.1 to 3.0 wt%, this superalloy is provided with an outstandingly high ductility.

[0014] In a second embodiment of the present invention, there is provided an Ni-base superalloy having a composition, in percent (%) by weight, of: 0.16-0.3% of C, 0.016-0.05% of B, 1.4-3.0% of Hf, 10.2-25% of Co, 1-4.9% of Ta, 1.5-8 wt% of Cr, 0-0.95% of Mo, 7.2-15% of W, 3.5-6.5% of Al, 1.1-9 wt% of Re, 0.2-2% of Nb, 0-1% of V, 0-0.02% of Zr, 0-2% of at least one of platinum group elements, 0-2% of at least one of rare earth elements, 0-0.1% of at least one of alkaline earth metals and Si, and 0-5% of at least one element selected from Fe, Ga and Ge, and the balance consisting of Ni and unavoidable impurities. This alloy is particularly suited for use for conventional castings.

[0015] In the Ni-base superalloy in the second embodiment of the present invention, it is possible to improve high-temperature strength while maintaining excellent ductility when Cr is contained in an amount of 1.5 to 7 wt% and W in an amount of 9 to 15 wt%. When it is desired to obtain further improvement of high-temperature strength, it is suggested to contain Cr in an amount of 1.5 to 7 wt% and W in an amount of 11.2 to 15 wt%. In the Ni-base superalloy for conventional castings according to the second embodiment of the present invention, outstandingly high strength and ductility can be obtained when C is contained in an amount of 0.18 to 0.3 wt%, Hr in an amount of 1.8 to 3.0 wt%, Cr in an amount of 1.5 to 7 wt% and W in an amount of 11.2 to 15 wt%.

[0016] In a third embodiment of the present invention, there is provided an Ni-base superalloy comprising, in percent (%) by weight, 0.06 to 0.3% of C, 0.01 to 0.05% of B, 1.4 to 3.0% of Hf, 10.2 to 25% of Co, 1 to 12% of Ta, 1.5 to 16% of Cr, 0 to 0.95% of Mo, 7.2 to 15% of W, 3.5 to 6.5% of Al, 1.1 to 9% of Re, 0.2 to 2% of Nb, 0 to 1% of V, 0 to 0.02% of Zr, 0 to 2% of at least one of platinum group elements, 0 to 2% of at least one of rare earth elements, 0 to 0.1% of at least one of alkaline earth metals and Si, and 0 to 5% of at least one element selected from Fe, Ga and Ge, and the balance consisting of Ni and unavoidable impurities. This alloy is especially suited to be used for directionally solidified castings.

[0017] In the Ni-base superalloy in the third embodiment of the present invention, both high-temperature strength and oxidation resistance are found to excel when the content of Ta is adjusted to be 1 to 6.5 wt% and the content of W to be 9 to 15 wt%. Particularly high-temperature strength is maximized when Ta is 1 to 6.5 wt% and W is 10.5 to 15 wt%. In use for directionally solidified castings, in order to attain a further improvement of high-temperature strength while maintaining oxidation resistance, preferably the Ta content is adjusted to be 1 to 4.9 wt% and the W content to be 11.2 to 15 wt%. Most preferably the total content of Ta and W is made 15 to 17 wt%, with the W/(W + Ta) ratio being adjusted to be 0.6-0.8.

[0018] The Ni-base superalloys according to the present invention are provided with high high-temperature strength and ductility by subjecting them to a solution heat treatment and an aging treatment. The solvus temperature of the Ni-base superalloys of the present invention is 1,240°C or below and their incipient melting temperature is 1,260°C or above. Here, the "solvus temperature" is defined as the temperature at which the γ' phase, which is a precipitation strengthening phase, is dissolved into the γ phase in the dendrite core portion. The "incipient melting temperature" is the temperature at which melting of the eutectic portion, where the low-melting-point elements segregated during casting, begins. The solution heat treatment that can maximize the strength of the alloys is carried out at a temperature which is not lower than the solvus temperature and not higher than the incipient melting temperature. It is preferable that the gap between the solvus temperature and the incipient melting temperature is not less than 20°C, and the alloys of the present invention are advantageous in this point, too.

[0019] The castings of the Ni-base superalloys of the present invention are suited for application to the blades of industrial axial flow gas turbines or the centrifugal wheels for turbo chargers or microturbines. The directionally solidified castings or single crystal castings produced by the directional solidification method are particularly suited for making those of the axial flow gas turbine blades which are large in size and complicated in configuration. Although the term "blade" means a rotating blade, the castings of the Ni-base superalloys of the invention are also suited for application to the stationary vane. In carrying out casting according to the selector method or the seed crystal method using an Ni-base supperalloy of the present invention, it is possible to obtain a casting of which the important portion alone is composed of single crystal, with the grain boundaries being allowed to exist in other portions which are relatively low in importance. Since the alloys of the present invention are provided with both high solidification direction strength (intergranular strength) and high grain boundary strength, they are suited for applications where the important portion alone is composed of single crystal and the other portions are allowed to have grain boundaries.

[0020] The alloys of the present invention are prepared into a master ingot adjusted in its composition, then divided into a proper size and subjected to casting.

[0021] In producing a centrifugal wheel for turbo chargers or microturbines with an Ni-base superalloy of the present invention, casting is preferably carried out in such a manner that the surface of the blade portion will be composed of fine grains, the portion extending from the blade portion toward the hub portion will be composed of columnar grains oriented in the direction of solidification from the blade portion toward the hub portion, and the hub portion will be composed of coarse grains with a grain size of 5 mm or greater. This makes it possible to obtain the castings with few defects at low cost. Preferably the casting operation is of a formula in which the melt in contact with the solidification front is continuous all the way to the gate in the whole region of the product. Also, after casting, preferably an HIP treatment is conducted for 2 hours or longer under the conditions of 1,185 to 1,285°C with above 120 to 185 MPa prior to the solution treatment. This can reduce the casting defects of the product. The "fine grains" are the grains with a grain size smaller than 1 mm, and they include chill grains.

Brief Description of the Drawings

[0022]

FIG. 1 shows the grain texture of a DS plate.

FIG. 2 is a graph showing the relationship between creep rupture time in the solidification direction in DS castings and the Co content.

FIG. 3 is a graph showing the relationship between creep rupture time in the direction perpendicular to the solidification direction in DS castings and the Hf content.

FIG. 4 is a graph showing the relationship between creep rupture time in the solidification direction in DS castings and the W/(W + Ta) ratio.

FIG. 5 is a graph showing the relationship between creep rupture time in the direction perpendicular to the solidification direction in DC castings and the W/(W + Ta) ratio.

FIG. 6 is a graph showing the relationship between room-temperature tensile elongation in the direction perpendicular to the solidification direction in DS castings and the W/(W + Ta) ratio.

FIG. 7 is a graph showing the influence of the W/(W + Ta) ratio on the creep rupture time in the solidification direction in DS castings.

FIG. 8 is a graph showing the results of an oxidation test conducted on a DS casting of alloy 1092 and comparative castings.

FIG. 9 is a graph showing the results of a hot corrosion test conducted on a DS casting of alloy 1092 and comparative castings.

FIG. 10 is a graph showing the relationship between creep rupture time of CC castings and the Hf content.

FIG. 11 is a graph showing the relationship between creep rupture time of CC castings and the C content.

FIG. 12 is a graph showing the results of an oxidation test conducted on a CC casting of alloy 1081 and comparative castings.

FIG. 13 is a graph showing the results of a hot corrosion test conducted on a CC casting of alloy 1081 and comparative castings.

FIG. 14 is a perspective view of a rotating blade for industrial axial flow gas turbines.

FIG. 15 is a scheme showing the sectional grain texture of a centrifugal wheel for microturbines.

FIG. 16 is a diagram showing the relationship between the contents of Ta and W and creep rupture time in the DS-L direction in DS castings.

FIG. 17 is a diagram showing the relationship between the contents of Hf and C and creep rupture time in CC castings.

(Description of Reference Numeral)

1: rotating blade for industrial axial flow gas turbines

Detailed Description of the Invention

[0023] The effects and proper contents of the individual elements in the Ni-base superalloys according to the present invention will be described.

[0024] C has an effect of strengthening the grain boundaries as it forms MC type carbides with Hf, Ta, Nb, etc., or $M_{23}C_6$ and M_6C type carbides with Cr, Wr, Mo, etc., and serves for preventing movement of grain boundaries under high temperatures. It is thus an element which plays a particularly important role in the present invention. For producing such an effect, it is necessary that this element be contained in an amount of at least 0.06% or more. In case where a higher grain boundary strength is required in the conventional castings, this element is preferably contained in an amount of 0.09% or more, more preferably 0.16% or more. In case it is desired to improve both of strength and ductility in the conventional castings, C is preferably added in an amount of 0.18% or more. When carbon is added in an amount of 0.18% or more, the carbides are solidified out or precipitated at all of the grain boundaries and prevent the grain boundaries from moving during the HIP treatment or solution heat treatment and in the course of deformation, producing a remarkable effect of enhancing high-temperature strength and ductility. It should be noted, however, that too much addition of C rather causes a reduction of high-temperature strength since the elements effective for solid-solution reinforcement of the γ phase and γ' phase are taken away by the carbides. Also, addition of an excess amount of carbon results in reducing fatigue strength. Therefore, the upper limit of C needs to be set at 0.3%.

[0025] B is an element having an effect of increasing the binding force of the grain boundaries as it fills up the area of disconformity of the grain boundaries. In the alloys of the present invention, it is necessary to add this element in an amount of at least 0.01%. In case even a higher grain boundary strength is required in a conventional casting, it is desirable that this element be contained in an amount of 0.016% or more. However, since B may cause an excessive reduction of melting point of the Ni-base superalloys, this element should not be contained in a greater amount than 0.05%.

[0026] Hf segregates at the grain boundaries to serve for improving ductility at the grain boundaries. An improvement of solidification direction strength of the DS castings can be attained by enhancing intergranular strength of the castings. However, when the intergranular strength of the castings is enhanced so much as to largely exceed the grain boundary strength, the grain boundary strength is lowered relatively, causing an excessive reduction of ductility in the direction perpendicular to the solidification direction, or the direction perpendicular to the grain boundary, resulting in a reduction of strength in that direction. Also, in the case of conventional castings, if both of grain boundary strength and ductility are low, it is impossible to enhance the strength of the whole casting no matter how much the intergranular strength is increased. Hf is an essential element for preventing such a phenomenon from occurring, and it is contained in an amount of at least 0.2%, preferably 0.5% or more. Where importance is attached to ductility, this element is preferably contained in an amount of 1.1% or more for both conventional castings and directionally solidified castings, and in case high grain boundary strength is required, said element is preferably added in an amount of 1.4% or more. When Hf is added 1.8% or more, the areal ratio of the eutectic texture increases to enhance the effect of preventing movement of the grain boundaries like the carbides, resulting in an elevation (improving) of grain boundary strength. This setting is particularly effective for the conventional castings. However, excessive addition of this element lowers the melting point of the alloys as in the case of B, so that it needs to hold its addition to an amount of 3.0% or below.

[0027] Co has the effect of lowering the solvus temperature of the γ' phase to facilitate the solution heat treatment. Particularly when it is used for partial solid solution as in the case of the alloys of the present invention, it is possible to enlarge the area where the γ' phase is dissolved into the γ phase during solution heat treatment even at a low heat treatment temperature. For obtaining such an effect, this element needs to be contained in an amount of at least 10.2%. However, excessive addition of Co makes the γ' phase unstable, resulting in a reduced strength of the alloy. Therefore, the amount of Co added should not exceed 25%.

[0028] Ta excels Ti and Nb as a solid solution strengthening element for the γ' phase and is therefore an element of worth. The greater the content of this element, the more enhanced the strength in the solidification direction, and it needs to be contained in an amount of at least 1%. However, excessive addition of this element worsens phase stability of the alloy, rather causing a reduction of its strength. Therefore, the content of this element should be restricted to 12% at the most. As another point of the present invention, it was disclosed that ductility of the castings can be improved by increasing the amount of W while relatively reducing the amount of Ta. Generally, the greater the combined amount of W and Ta, the more enhanced the strength of alloys, but on the other hand, if the combined amount exceeds a certain level, the TCP phase precipitates to rather work for lowering alloy strength. Therefore, in order to realize high strength and high ductility, it is suggested to make a composition in which the content of W is increased while the content of Ta is reduced correspondingly. The content of Ta is preferably restricted to 6.5% or less, especially 4.9% or less.

[0029] W, contrary to Ta, is an element conducive to solid solution strengthening of the γ phase. Therefore, the higher the content of this element, the more effective for enhancing the alloy strength. This element needs to be contained in an amount of at least 2%. Further, in order to satisfy both requirements for high strength and high ductility, it is expedient to make a composition in which W is higher in content than Ta. It is appropriate to contain W in an amount of 7.2% or more, preferably 9% or more, more preferably 11.5% or more. However, as in the case of Ta, excess addition of W may affect phase stability of the alloy to cause precipitation of the harmful phases such as TCP phase and a sizable reduction of hot corrosion resistance, so that the content of this element should be defined not to exceed 15%.

[0030] Since W and Ta are substantially equal in mass number, they are almost same in atomic percent and weight percent which are the important factors for indicating the alloy characteristics. An alloy excelling particularly in strength and ductility could be obtained when the W/(W + Ta) ratio was in the range of 0.6 to 0.8. Also, saliently high strength could be obtained when the total content of Ta and W was 15 to 17%.

[0031] Mo is an element of the same group as W, therefore almost same as W in its effects to the various properties of the Ni-base superalloys. But the present inventors found that Mo, in comparison with W, may excessively deteriorate hot corrosion resistance in a combustion environment. Therefore, the content of this element in the alloys of the present invention is limited to 0 to 0.95%.

[0032] Re, like W and Mo, is also an element which serves principally for solid solution strengthening of the γ phase. This element, as compared with Mo and W, does not deteriorate hot corrosion resistance in the combustion environment and is therefore a very useful element for satisfying both requirements for hot corrosion resistance and high-temperature strength, so that by substituting W or Mo with this element, it is possible to strengthen the alloy while improving its corrosion resistance at the same time. For obtaining this effect, it is necessary to contain this element in an amount of at least 0.5%, preferably 1.1% or more. This element, however, may exert influence on the phase stability because of very low rate of distribution to the γ' phase side, so that it needs to restrict its content to 9% at most.

[0033] Cr is an essential element for maintaining hot corrosion resistance of the Ni-base superalloys by forming a protective film of Cr_2O_3. This element, therefore, needs to be contained in an amount of at least 1.5%. However, excess addition of this element, like W, adversely affects phase stability of the alloy and may cause precipitation of the harmful phases such as TCP phase, so that its content should be defined not to exceed 16%. In case where importance is attached to high-temperature strength and it needs to accordingly increase the contents of W and Re, the content of Cr is lessened to 8% or less, and where even greater importance is given to high-temperature strength, the content of this element is cut to 7% or less.

[0034] Al is an essential element for forming the γ' phase (Ni_3Al), and it needs to be contained in an amount of at least 3.5%. In case it is desired to increase the volume ratio of the γ' phase and preference is given to the strength in the solidification direction of the DS casting, this element is preferably contained in an amount of 5% or more. Al also serves for improving oxidation and hot corrosion resistance of the alloy by forming a protective film of Al_2O_3. Excessive addition of this element, however, causes a drop of the degree of solid solution strengthening of the γ' phase and rather serves for decreasing high-temperature strength of the alloy, so that its amount added should be restricted to 6.5% at most.

[0035] Nb, although less effective than Ti, has an effect of preventing formation of composite oxides of Cr and Al and improving hot corrosion resistance of the alloy. On the other hand, this element is higher than Ti, though lower than Ta, in the effect of solid solution strengthening of the γ' phase. Thus, Nb is an element useful for improving hot corrosion resistance with no compromise in high-temperature strength, and it needs to be contained in an amount of 0.2% or more. However, for maintaining stability of the γ' phase, the content of Nb should not exceed 2%. Where importance is attached to hot corrosion resistance in particular, this element is preferably added in an amount of 0.5% or more.

[0036] Ti has the effect of preventing formation of composite oxides of Cr and Al to improve hot corrosion resistance of the alloys. In case where both of Ta and Nb are contained as in the alloy system of the present invention, stability of the γ' phase may be impaired if Ti is further added. Also, when the balance of strength and hot corrosion and oxidation resistance is taken into consideration, it is preferred to add Nb or Ta rather than Ti. Further, for the alloy systems, like that of the present invention, which have a tendency to lower in incipient melting temperature because of incorporation of a grain boundary strengthening element, it is effective for improving solid solution treatment efficiency to optimize the balance of the alloy elements and raise incipient melting temperature of the alloys as much as possible, and this leads to an enhancement of strength of the alloys. In the comparison of Ta, Nb and Ti in their effect of lowering incipient melting temperature of the alloys per 1 atomic %, such effect is found higher in the order of Ta<Nb<Ti, from which it can be noted that addition of Ti is undesirable for improving incipient melting temperature of the alloys. So, Ti is not contained in the alloys of the present invention. With the alloys of the present invention, it has become possible to obtain excellent properties by controlling the balance of W which is placed on the γ phase side and Ta which is placed on the γ' phase side as mentioned above, and a particularly good result could be obtained where the content of Ta was low. Therefore, if Ti which is also placed on the γ' phase side is added, it is necessitated to further reduce the content of Ta which is the most effective for improving high-temperature strength in the elements on the γ' phase side which are held low in content from the beginning. In this respect, too, it is important to exclude Ti from the alloys of the present invention.

[0037] Zr, like Hf, has been credited with the effect of enhancing grain boundary strength, but the studies by the present inventors disclosed that Zr is by far smaller than Hf in its effect on the enhancement of grain boundary strength. Further, as in the case of the relation between Ta, Nb and Ti described above, the effect of Zr on lowering incipient melting temperature is greater than that of Hf. Thus, in view of the fact that Zr is smaller than Hf in the effect of enhancing grain boundary strength while it is greater than Hf in the effect of lowering incipient melting temperature, there is found no significance in adding this element in the alloys. Addition of Zr necessitates a substantial decrease of the content of Hf which is one of the important elements in the alloys of the present invention. Therefore, in the alloys of the present invention, the content of Zr was restricted to 0 to 0.02%, the same level as the impurities. This made it possible to increase the content of Hf and to realize an enhancement of grain boundary strength.

[0038] Addition of V lowers the solid solution limit of Ta and Nb, resulting in a reduction of high-temperature strength. It also greatly lowers hot corrosion resistance. In the alloys of the present invention, therefore, the content of this element is defined to the impurity level of 0 to 1%.

[0039] The rare earth elements such as Y are of service to the improvement of adhesion of the Al_2O_3 protective film to greatly improve oxidation resistance. But these elements excessively lower the melting point of the Ni-base superalloys, so that their content should be restricted to 0 to 2%. The rare earth elements usable in this invention are the elements belonging to the group 3A of the periodic table and include, beside Y, lanthanoids such as Sc, La and Ce and actinoids such as Ac. The effect of these elements is almost the same and remains substantially unchanged no matter whether they are used singly or in combination of two or more. In the present invention, therefore, the total content of these elements is limited to 0 to 2%.

[0040] The alkaline earth metals and Si have the effect of improving adhesion of the oxide film, but excessive addition of these elements lowers ductility at the grain boundaries. So, these elements are contained preferably in a total amount of 0 to 0.1%.

[0041] The platinum group elements such as Pt and Ru have a function to widen the solid solution limit of W, Re, etc., which are the effective elements for enhancing high-temperature strength, but since these elements are very expensive, they are contained in a limited amount of 0 to 2%.

[0042] Fe, Ga and Ge have the effect of strengthening adhesion of the oxide film, and Ga and Ge contribute to enhancing high-temperature strength by forming intermetallic compounds with Ni, but excess addition of any of these elements adversely affects ductility at the grain boundaries, so that their content is restricted to 0 to 5% in total.

EXAMPLES

[0043] Described in the following are the processes of producing the directionally solidified castings and conventional castings, preparation of the specimens, and the results of measurements of their strength and ductility. The compositions of the Ni-base superalloys used in the tests are shown in Table 1. Alloy 1061 is an alloy included in the ambit of compositions of USP 6,051,083 alloys. Alloys 1064-1066, 1071-1073, 1077, 1079-1081, and 1086-1104 are the alloys of the present invention used in the Examples.

Table 1

No.	ALLOY COMPOSITION (mass%)													
	Cr	Al	Ti	W	Mo	Ta	Nb	Re	Co	Hf	Zr	C	B	Ni
alloy 1061	7.10	5.10	0.00	8.78	0.80	8.88	0.81	1.44	1.00	0.25	0.00	0.07	0.02	REMAINDER
alloy 1062	7.12	5.11	0.00	8.50	0.80	8.58	0.80	1.41	4.75	0.25	0.00	0.07	0.02	REMAINDER
alloy 1063	7.15	5.13	0.00	8.14	0.81	8.25	0.81	1.41	9.58	0.25	0.00	0.07	0.02	REMAINDER
alloy 1064	7.19	5.15	0.00	8.14	0.80	7.45	0.80	1.44	10.31	1.13	0.00	0.07	0.02	REMAINDER
alloy 1065	7.19	5.16	0.00	8.13	0.82	6.94	0.81	1.41	10.32	1.54	0.00	0.07	0.02	REMAINDER
alloy 1066	7.16	5.14	0.00	8.12	0.80	6.40	0.80	1.42	10.35	2.01	0.00	0.07	0.02	REMAINDER
alloy 1071	7.53	5.12	0.00	6.21	0.81	8.50	0.86	1.44	10.36	1.51	0.00	0.07	0.02	REMAINDER
alloy 1072	7.01	5.13	0.00	9.89	0.81	5.31	0.83	1.44	10.37	1.54	0.00	0.07	0.02	REMAINDER
alloy 1073	6.77	5.15	0.00	11.45	0.81	3.71	0.86	1.44	10.51	1.55	0.00	0.07	0.02	REMAINDER
alloy 1077	6.76	5.13	0.00	12.16	0.83	3.70	0.86	1.44	10.42	1.54	0.00	0.07	0.02	REMAINDER
alloy 1079	6.73	5.11	0.00	12.10	0.83	3.89	0.85	1.43	10.37	2.04	0.00	0.07	0.02	REMAINDER
alloy 1080	6.73	5.11	0.00	12.10	0.83	3.89	0.85	1.43	10.37	2.04	0.00	0.15	0.02	REMAINDER
alloy 1081	6.73	5.11	0.00	12.10	0.83	3.89	0.85	1.43	10.37	2.04	0.00	0.20	0.02	REMAINDER
alloy 1086	6.98	5.12	0.00	10.59	0.83	5.30	0.86	1.44	10.45	1.54	0.00	0.07	0.02	REMAINDER
alloy 1087	6.95	5.09	0.00	10.54	0.83	5.99	0.85	1.43	10.41	1.53	0.00	0.07	0.02	REMAINDER
alloy 1088	6.97	5.11	0.00	10.57	0.83	6.01	0.85	1.44	10.43	1.03	0.00	0.07	0.02	REMAINDER
alloy 1089	6.98	5.12	0.00	9.85	0.83	6.02	0.86	1.44	10.45	1.54	0.00	0.07	0.02	REMAINDER
alloy 1090	6.98	5.12	0.00	9.85	0.83	5.30	0.86	2.93	10.46	1.03	0.00	0.07	0.02	REMAINDER
alloy 1091	6.98	5.11	0.00	10.59	0.83	5.29	0.86	1.44	14.12	1.54	0.00	0.07	0.02	REMAINDER
alloy 1092	6.76	5.13	0.00	12.16	0.83	3.70	0.86	1.44	10.44	1.54	0.00	0.07	0.02	REMAINDER
alloy 1093	6.73	5.11	0.00	12.10	0.83	4.41	0.85	1.43	10.39	1.53	0.00	0.07	0.02	REMAINDER
alloy 1094	6.75	5.12	0.00	12.14	0.83	4.42	0.85	1.44	10.38	1.03	0.00	0.07	0.02	REMAINDER
alloy 1095	6.76	5.13	0.00	11.42	0.83	4.43	0.86	1.44	10.43	1.54	0.00	0.07	0.02	REMAINDER
alloy 1096	5.06	5.16	0.00	10.38	0.86	3.74	0.83	4.34	10.83	1.00	0.00	0.07	0.02	REMAINDER

(continued)

No.	ALLOY COMPOSITION (mass%)													
	Cr	Al	Ti	W	Mo	Ta	Nb	Re	Co	Hf	Zr	C	B	Ni
alloy 1097	6.76	5.13	0.00	12.15	0.83	3.70	0.86	1.44	14.12	1.54	0.00	0.07	0.02	REMAINDER
alloy 1098	5.02	5.59	0.00	8.48	0.87	3.93	0.85	4.25	10.52	1.00	0.00	0.07	0.02	REMAINDER
alloy 1099	6.77	5.11	0.00	12.10	0.83	3.89	0.85	1.43	10.30	2.04	0.00	0.07	0.02	REMAINDER
alloy 1100	6.75	5.11	0.00	12.12	0.83	3.83	0.85	1.43	10.30	2.04	0.00	0.15	0.02	REMAINDER
alloy 1101	6.76	5.11	0.00	12.14	0.83	3.82	0.85	1.43	10.30	2.04	0.00	0.20	0.02	REMAINDER
alloy 1102	6.72	5.11	0.00	12.09	0.83	3.84	0.85	1.43	10.30	1.50	0.00	0.15	0.02	REMAINDER
alloy 1103	6.71	5.11	0.00	12.08	0.83	3.89	0.85	1.43	10.30	1.50	0.00	0.20	0.02	REMAINDER
alloy 1104	5.02	5.59	0.00	8.48	0.87	3.93	0.85	4.25	10.30	2.04	0.00	0.20	0.02	REMAINDER
alloy 1201	6.73	5.11	0.00	12.10	0.83	3.89	0.85	1.43	10.37	2.04	0.00	0.05	0.02	REMAINDER
14%Cr alloy	14.00	3.00	5.00	4.00	4.00	0.00	0.00	0.00	9.50	0.00	0.03	0.17	0.015	REMAINDER
USP3,720,509	8.3	5.6	1.0	10.0	0.7	3.0	0.0	0.0	10.0	1.4	0.04	0.07	0.015	REMAINDER
USP5,069,873	6.0	5.7	0.7	8.0	0.5	3.0	0.0	3.0	9.0	1.4	0.007	0.07	0.015	REMAINDER

[0044] The castings used for the evaluation were the 100 mm x 15 mm x 130 mm flat plates, and either or both of conventional castings (CC) and directionally solidified castings (DS) were produced. Using the master ingots prepared in advance to have the compositions shown in Table 1, the CC plates were produced by conventional vacuum casting while the DS plates were produced by a mold withdrawal type directional solidification method. The castings were subjected to a solution heat treatment and an aging, and then the evaluation test pieces (specimens) were made therefrom by machining. The CC specimens were subjected to an HIP treatment prior to the solution heat treatment. The HIP treatment was carried out in Ar for 4 hours under the conditions of 1,200°C and 150 MPa. The solution heat treatment (ST) was conducted at a temperature above the solvus and below the incipient melting temperature as standards. The solution heat treatment was followed by rapid cooling by gas blowing. For some of the alloys having a large gap between solvus temperature and incipient melting temperature, there were prepared the test pieces for several different ST temperatures. The aging was a two-stage heat treatment in which each alloy was first heated at 1,080°C for 4 hours, then rapidly cooled down to room temperature, and again heated at 871°C for 20 hours, followed by rapid cooling to room temperature.

[0045] FIG. 1 shows the grain texture of a DS plate. In FIG. 1 are shown the solidification direction, a grain boundary and the direction perpendicular to the solidification direction. With the DS specimens, creep rupture strength in the solidification (DS-L) direction and the direction (DS-T direction) perpendicular to the solidification direction was measured. Creep rupture strength in the DS-L direction was evaluated by measuring the creep rupture time under the conditions of 850°C and 40 kgf/mm^2 or 1, 040°C and 14 kgf/mm^2. Creep rupture strength in the DS-T direction was evaluated by measuring the creep rupture time under the conditions of 982°C and 14 kgf/mm^2. Since the CC plates were equiaxis grains, the direction of collection of the specimens was not specified but they were collected from the arbitrary sections. Creep rupture strength of the CC specimens was evaluated by measuring the creep rupture time under the conditions of 982°C and 14 kgf/mm^2. The specimen geometry and the testing conditions for the creep and tensile tests followed the ASTM or JIS standards. Hot corrosion resistance was evaluated by a 900°C burner rig test for both DS and CC specimens. The degree of hot corrosion resistance was judged by the time required till the change in amount (weight) due to hot corrosion reached 20 mg/cm^2. Each test was conducted cyclically with 10 hours as one cycle time, and the amount of change in weight was measured at the end of each cycle of test. Heavy oil containing 0.06 mass% of sulfur was used as fuel, and in order to accelerate hot corrosion, a 0.1 mass% NaCl solution was sprayed to the combustion gas at a rate of 30 cc/min. For the evaluation of oxidation resistance, the 10 mm x 15 mm x 3 mm flat plates were used for both DS and CC castings. These plates were heated in the atmosphere at 1,100°C for 100 times per cycle, and the change in weight was measured at the end of each cycle, with the grade of oxidation resistance being determined from the absolute value of said change in weight. Each test was conducted through a maximum of 10 cycles, for a total period of 1,000 hours at longest.

[0046] First, the results of evaluation on the DS specimens are explained.

[0047] Table 2 shows the creep rupture time of the alloys 1061-1063 in the DS-L direction, and FIG. 2 shows the relationship between creep rupture time in the DS-L direction and Co content in these alloys. It is seen that the longer the creep rupture time, the higher the creep rupture strength. Alloy 1061 was developed as a single crystal (SC) alloy, so this alloy, when cast into a DS casting, proves low in creep rupture strength in the DS-L direction. In comparison with this alloy 1061, the other alloys increased in Co content show high creep rupture strength in the DS-L direction. In the case of alloy 1063 which contains about 10% of Co, it was confirmed that its creep rupture time was more than 4 times longer than that of alloy 1061.

[0048] Table 3 shows creep rupture time in the DS-T direction of alloy 1063 and alloys 1064-1066 which were increased in Co and Hf contents in comparison with alloy 1063, and FIG. 3 shows the relationship between creep life in the DS-T direction and Hf content in these alloys. Alloy 1063 is high in creep rupture strength in the DS-L direction but low in said strength in the DS-T direction, that is, low in strength at grain boundaries. It was found that, in comparison with alloy 1063, creep rupture strength in the DS-T direction can be greatly enhanced by slightly increasing the Co content and further increasing the Hf content.

[0049] From the foregoing, it was confirmed that creep rupture strength in both DS-L direction and DS-T direction could be boosted by increasing both of Co content and Hf content over alloy 1061, specifically by making the Co content 10.2% or higher and the Hf content 0.5% or higher, preferably 1.1% or higher.

Table 2

ALLOYS	Co (mass%)	DS-L DIRECTION 850°C-40 kgf/mm^2 CREEP RUPTURE TIME (h)	ST TEMPERATURE (°C)
alloy 1061	1.0	504	1280
alloy 1062	4.8	1222	1280
alloy 1063	9.6	2229	1280

Table 3

ALLOYS	Hf (mass%)	DS-T DIRECTION 982°C-14 kgf/mm^2 CREEP RUPTURE TIME (h)	ST TEMPERATURE (°C)
alloy 1063	0.3	214	1260
alloy 1064	1.1	1188	1260
alloy 1065	1.5	1170	1250
alloy 1066	2.0	1003	1250

[0050] As it was thus confirmed that the DS castings of the Ni-base superalloys containing Co and Hf in high ratios are high in strength in both DS-L direction and DS-T direction, investigations were then made into the contents of W and Ta.

[0051] W is an element which is placed principally on the γ phase side while Ta is an element placed principally on the γ' phase (precipitation phase) side. The alloys with a high W content are increased in lattice constant on the γ phase side, and the lattice constant mismatch generally defined by the formula: (lattice constant of γ' phase - lattice constant of γ phase)/(average lattice constant of both phases) is lessened. The lattice constant mismatch is an important factor which greatly influences the deformation mechanism of the Ni-base superalloys.

[0052] Table 4 shows the DS-L direction 850°C-40 kgf/mm^2 creep rupture time of the alloy 1065, which has been confirmed to have high DS-T direction creep rupture strength from the results of Table 3, and the alloys 1071-1073. FIG. 4 shows the relationship between the W/(W + Ta) ratio (in percent by weight) and the DS-L direction 850°C-40 kgf/mm^2 creep rupture time of these alloys. Also, Table 5 shows the DS-T direction 982°C-14 kgf/mm^2 creep rupture time of these alloys, and FIG. 5 shows the relationship between the W/(W + Ta) ratio and the DS-T direction 982°C-14 kgf/mm^2 creep rupture time.

[0053] The above results endorse that the greater the W/(W + Ta) ratio, the more enhanced the creep rupture strength in both DS-L direction and DS-T direction. The DS-L direction 850°C-40 kgf/mm^2 creep rupture time, 2,654 hours, of the alloy 1073 exceeds that (2,470 hours) of the single crystal (SC) castings of the alloy 1061 tested under the same conditions.

[0054] From the foregoing, it has been confirmed that, as compared with the alloy 1061, those alloys which were increased in Co and Hf contents and had their W/(W + Ta) ratio adjusted to fall in the range of 0.6 to 0.8 have high grain boundary strength (DS-T direction strength) while maintaining the same level of DS-L direction creep rupture strength as the SC castings of the alloy 1061 and are suited for use in making a large-sized blade of complicate shape. Particularly it was found that, as apparent from the creep characteristics of the alloy 1073, the alloys in which the W content exceeds 11% while the Ta content is below 4% are outstandingly high in strength in both DS-L and DS-T directions and possess the best available properties.

[0055] Table 6 shows DS-T direction room temperature tensile elongations of the alloy 1065 and alloys 1071-0173, and FIG. 6 shows the relationship between DS-T direction room temperature tensile elongation and W/(W + Ta) ratio of these alloys. Any of these alloys showed room temperature tensile elongation of greater than 3%, verifying their high ductility. The best room temperature ductility was provided when the W/W + Ta ratio was around 0.65, and it has been confirmed that it was preferable to adjust the W/(W + Ta) ratio to stay in the range of 0.6 to 0.8 for the improvement of ductility, too.

Table 4

ALLOYS	W (mass%)	Ta (mass%)	W/(W+Ta)RATIO (in % by mass)	DS-L DIRECTION 850°C-40 kgf/mm^2 CREEP RUPTURE TIME (h)	ST TEMPERATURE (°C)
alloy 1071	6.21	8.50	0.42	1209	1270
alloy 1065	8.13	6.94	0.54	1970	1270
alloy 1072	9.89	5.31	0.65	1964	1270
alloy 1073	11.45	3.71	0.76	2654	1260

Table 5

ALLOYS	W (mass%)	Ta (mass%)	W/(W+Ta)RATIO (in % by mass)	DS-T DIRECTION 982°C-14 kgf/mm^2 CREEP RUPTURE TIME (h)	ST TEMPERATURE (°C)
alloy 1071	6.21	8.50	0.42	867	1250
alloy 1065	8.13	6.94	0.54	1170	1250
alloy 1072	9.89	5.31	0.65	1368	1250
alloy 1073	11.45	3.71	0.76	1521	1240

Table 6

ALLOYS	W (mass%)	Ta (mass%)	W/(W+Ta)RATIO (in % by mass)	ROOM TEMPERATURE TENSILE ELONGATION IN DS-T DIRECTION (%)	ST TEMPERATURE (°C)
alloy 1071	6.21	8.50	0.42	3.4	1250
alloy 1065	8.13	6.94	0.54	4.0	1250
alloy 1072	9.89	5.31	0.65	8.1	1250
alloy 1073	11.45	3.71	0.76	3.9	1240

[0056] DS-L direction and DS-T direction creep rupture strength was evaluated with several types of Ni-base superalloys in which the W/(W + Ta) ratio by weight was within the range of 0.6 to 0.8. The DS-L direction creep rupture strength was measured under the two different conditions: 850°C-40 kgf/mm^2 and 1,040°C-14 kgf/mm^2. Table 7 shows the results of evaluations on alloys 1072, 1073 and 1086-1098, and FIG. 7 shows the relationship between DS-L direction 1,040°C-14 kgf/mm^2 creep rupture time and W/(W + Ta) ratio of these alloys. The results of Table 7 and FIG. 7 confirm an enhancement of strength in these alloys except for the alloys 1091 and 1097 in which the Co content was increased to more than 14% on the basis of the alloys 1072 and 1073. These results teach that the Co content should rather be held below 14%. Among the alloys in which the Re content was in the order of 1.4%, the alloy 1093 which was increased in W and Ta contents as compared with the alloy 1073 was the highest in creep rupture strength. However, in view of long-time phase stability, the alloy 1092 increased in W content from the level of alloy 1073 is considered more preferable. The alloys 1090, 1096 and 1098 increased in content of Re which is an exorbitantly expensive element in comparison with W and Ta were outstandingly high in creep rupture strength, so that it was found that the increase of Re content is expedient where an enhancement of high-temperature strength is desired at the cost of high price. As regards Hf, in view of the fact that DS-T direction creep rupture time of the alloy 1088 is excessively short as compared with other alloys, it is considered advisable to add this element in an amount of up to 1.5% in case where greater importance is attached to strength in the DS-T direction.

[0057] FIG. 16 shows the relationship between Ta and W contents and DS-L direction creep rupture time of the alloys 1072, 1073 and 1086-1098. It is seen that creep rupture strength is high when the W/(W + Ta) ratio (in percent by weight) is 0.6 to 0.8, the W content is 10.5 to 15% and the Ta content is 1 to 6.5%, with particularly high strength being obtained when the total content of W and Ta is 15 to 17%.

Table 7

ALLOYS	W (mass%)	Ta (mass%)	W/(W+Ta) RATIO (mass%)	Co (mass%)	Hf (mass%)	Re (mass%)	DS-L DIRECTION 1040°C-14 kgf/mm^2 CREEP RUPTURE TIME (h)	DS-L DIRECTION 850°C-40 kgf/mm^2 CREEP RUPTURE TIME (h)	DS-T DIRECTION 982°C-14 kgf/mm^2 CREEP RUPTURE TIME (h)	ST TEMPERATURE (°C)
alloy 1072	9.89	5.31	0.65	10.37	1.54	1.44	226	1964	1200	1270
alloy 1073	11.45	3.71	0.76	10.51	1.55	1.44	232	2654	1466	1260
alloy 1086	10.59	5.30	0.67	10.45	1.54	1.44	288	2703	-	1250
alloy 1087	10.54	5.99	0.64	10.41	1.53	1.43	362	3377	960	1260
alloy 1088	10.57	6.01	0.64	10.43	1.03	1.44	453	2652	586	1260
alloy 1089	9.85	6.02	0.62	10.45	1.54	1.44	305	2257	1085	1260
alloy 1090	9.85	5.30	0.65	10.46	1.03	2.93	490	3395	1275	1260
alloy 1091	10.59	5.29	0.67	14.12	1.54	1.44	151	2591	1299	1260
alloy 1092	12.16	3.70	0.77	10.44	1.54	1.44	406	3174	1901	1260
alloy 1093	12.10	4.41	0.73	10.39	1.53	1.43	490	3721	1566	1260
alloy 1094	12.14	4.42	0.73	10.38	1.03	1.44	424	3604	-	1260
alloy 1095	11.42	4.43	0.72	10.43	1.54	1.44	358	3362	1812	1260
alloy 1096	10.38	3.74	0.74	10.83	1.00	4.34	621	4662	1475	1280
alloy 1097	12.15	3.70	0.77	14.12	1.54	1.44	225	2165	1156	1260
alloy 1098	8.48	3.93	0.68	10.52	1.00	4.25	508	3695	2096	1280

- Continued ...-

[0058] FIG..8 shows the results of an oxidation resistance test on a DS casting of the alloy 1092 and comparative castings. It is noted that this DS casting of the alloy 1092 is improved in oxidation resistance over both of the single crystal (SC) casting of the alloy 1061 and the 14% Cr alloy (CC casting) which has practically been used for the industrial gas turbine blades. FIG. 9 shows the results of a hot corrosion resistance test by a burner rig on a DS casting of the alloy 1092 and comparative castings. This alloy 1092 DS casting is improved in hot corrosion resistance in comparison with any of the alloy 1061 SC casting, the DS casting disclosed in USP 5,069,873 and the 14% Cr alloy CC casting which has practically been applied to the industrial gas turbine blades.

[0059] The results of evaluations on the CC castings are described below.

[0060] The centrifugal wheels of turbo chargers or microturbines require the CC castins. Table 8 shows the results of a creep rupture test on the CC castings of the alloys 1061, 1077 and 1079, and FIG. 10 shows the relationship between creep rupture time and Hf content in the CC castings of these alloys. It was confirmed that the CC castings of the alloys which were increased in Hf content relative to the CC castings of the alloy 1061 possessed high creep rupture strength.

[0061] So, the influence of C content on creep rupture strength was examined based on a CC casting of the alloy 1079 which was increased in Hf content and improved in creep rupture strength. Table 9 shows creep rupture time of the CC castings of the alloys 1079-1081, and FIG. 11 shows the relationship between creep rupture time and C content. It was certified that creep rupture strength could be further improved by increasing the C content above that of the alloy 1079 casting.

[0062] The alloy 1081 with a C content of 0.2%, which showed the highest strength among the alloys shown in Table 9, was evaluated by raising the ST temperature by 20°C to 1,260°C. As a result, the creep rupture time under the condition of 982°C and 14 kgf/mm^2 was 2,164 hours. This is equivalent to 898°C when converted to the 10^5 hour service temperature under a stress of 14 kgf/mm^2. This service temperature matches that of the so-called second generation DS alloys (alloy system containing 3% of Re) such as those disclosed in USP 5,069,873. It was found that since the CC castings of the alloys of a composition equivalent to the alloy 1081 have strength comparable with the second generation DS alloys, these CC castings can be very advantageously applied to the centrifugal wheels for turbo chargers and microturbines to which the DS alloys can hardly be applied. It was further found that the DS castings which have hitherto been predominantly used for the axial flow turbine blades can now be replaced by the CC castings, providing a very significant economical effect. As a result of evaluation of room temperature tensile ductility of the alloy 1081 at an ST temperature of 1,260°C, its elongation at rupture at room temperature was determined to be 5.3%, which indicates that this alloy possesses sufficient ductility in addition to high high-temperature strength. Alloy 1081 is almost equal to the DS casting alloy 1092 in content of the elements other than C and Hf. From the above, it is considered that high high-temperature strength can be obtained by properly selecting the Co content and W/Ta ratio as in the case of alloy 1092, and by further optimizing the Hf and C contents, there could be obtained the alloys best suited for application to the centrifugal wheels of turbo chargers or microturbines.

[0063] FIG. 12 shows the results of an oxidation resistance test on a CC casting of alloy 1081 and comparative castings. It can be seen that the alloy 1081 CC casting is improved in oxidation resistance in comparison with either of the alloy 1061 SC casting and the 14% Cr alloy CC casting which has practically been used for the industrial gas turbines. FIG. 13 shows the results of a burner rig hot corrosion test on a CC casting of alloy 1081 and comparative castings. It is noticed that the alloy 1081 CC casting is improved in hot corrosion resistance over any of the alloy 1061 SC casting, the DS casting of USP 5,069,873 and the 14% Cr alloy CC casting which has been practically used for the industrial gas turbines.

[0064] Table 10 shows the results of a 982°C-14 kgf/mm^2 creep rupture test conducted on the alloys with the compositions analogous to that of alloy 1081, specifically alloys 1099-1104. For the sake of comparison, there are also shown the test results on an alloy identical with that of USP 3,720,509. Among these alloys, alloy 1101 is the longest in creep rupture time. It was found that where the C and Hf contents were defined in the ranges of 0.15 to 0.2% and 1.50 to 2.04%, respectively, the compositions increased in both of C and Hf contents excelled in creep rupture strength. Alloy 1104 is smaller in W content and also lower in ST temperature than the alloys 1099-1103, so that this alloy is low in creep rupture strength in comparison to the alloys 1099-1103, but as a result of measurement of tensile elongation at rupture at room temperature, it was found that the said tensile elongation of this alloy was as high as 6.4%, which corroborates high usefulness of this alloy in applications where importance is attached to the strength at grain boundaries. Creep rupture strength of alloy 1104 is by far higher than that of the alloy of USP 3,720,509 which is widely used for the centrifugal whets of turbo chargers or microturbines.

Table 8

ALLOYS	Hf (mass%)	982°C-14 kgf/mm^2 CREEP RUPTURE TIME (h)	ST TEMPERATURE (°C)
alloy 1061	0.25	156	1240
alloy 1077	1.50	497	1240
alloy 1079	2.00	853	1240

Table 9

ALLOYS	C (mass%)	982°C-14 kgf/m^2 CREEP RUPTURE TIME (h)	ST TEMPERATURE (°C)
alloy 1201	0.05	814	1240
alloy 1079	0.07	853	1240
alloy 1080	0.15	1511	1240
alloy 1081	0.20	1638	1240

Table 10

ALLOYS	C (mass%)	Hf (mass%)	982°C-14 kgf/mm^2 CREEP RUPTURE TIME (h)	ST TEMPERATURE (°C)
USP3,720,509	0.07	1.4	252	1200
alloy 1099	0.07	2.04	898	1240
alloy 1100	0.15	2.04	1525	1240
alloy 1101	0.20	2.04	1640	1240
alloy 1102	0.15	1.50	1410	1240
alloy 1103	0.20	1.50	1521	1240
alloy 1104	0.20	2.04	1125	1200

[0065] FIG. 17 shows the relationship between Hf and C contents and 982°C-14 kgf/mm^2 creep rupture time with regards to alloys 1077, 1079 and 1099-1103. An outstandingly high creep rupture strength could be obtained when the Hf content was within the range of 1.4 to 3% and also not less than -10C + 3.4 and not greater than -10C + 4.4.

[0066] A 150 kg master ingot was cast with the composition of alloy 1092 to evaluate castability of a large-sized master ingot, finding that there was involved no problem in this matter. Further, by using this master ingot, an industrial axial flow gas turbine rotating blade 1 with an overall length of 230 mm shown in FIG. 14 was cast by the mold withdrawal type directional solidification method. The macrostructure and microstructure of this directionally solidified blade were examined, and then the casting was further subjected to fluorescent penetrant testing and x-ray inspection. It was confirmed as a result that there was no problem with castability of this alloy. Separately, another directionally solidified blade was subjected to a solution heat treatment in which the blade was heated in vacuum at 1,260°C for 4 hours and then rapidly cooled by blowing Ar gas, and thereafter further subjected to a two-stage aging in which the blade was similarly heated in vacuum at 1,080°C for 4 hours, then rapidly cooled down to room temperature, and then again heated at 871°C for 20 hours, followed by rapid cooling to room temperature. A specimen was collected from this blade and subjected to a creep rupture test. As a result, the DS-L direction creep rupture time under the conditions of 850°C and 40 kgf/mm^2 was 2,400 hours, which could well match that (2,470 hours) of the single crystal (SC) specimen of alloy 1061.

[0067] Similarly, a 150 kg master ingot was cast with the composition of alloy 1101, and its large-sized master ingot castability was evaluated, confirming that there was no problem in this respect. Also, by using this master ingot, a microturbine centrifugal wheel with a maximum blade diameter of 230 mm shown in FIG. 15 was cast by a conventional vacuum casting method. The macrostructure and microstructure of this wheel were examined, followed by fluorescent penetrant testing and X-ray inspection. The test results confirmed no problem with castability of this alloy. Separately, another wheel was cast similarly and subjected to a 4-hour HIP treatment in Ar under the conditions of 1,200°C and 150 MPa, after which it was further subjected to a solution heat treatment in which the wheel was heated in vacuum at 1,240°C for 4 hours and then rapidly cooled by blowing Ar gas, followed by a two-stage aging in which the wheel was similarly heated in vacuum at 1,080°C for 4 hours, then rapidly cooled to room temperature, again heated at 871°C for 20 hours and then rapidly cooled to room temperature. A specimen was collected from the greatest diameter portion at the center of this blade in the centrifugal stress direction, and its creep rupture strength was evaluated under the conditions of 982°C and 14 kgf/mm^2.

[0068] A similar microturbine centrifugal wheel was cast with the alloy of USP 3,720,509 by a conventional vacuum casting method. The casting was subjected to the same HIP treatment, solution treatment and two-stage aging treatment as conducted in the Examples of the present invention. A specimen was also collected from this wheel in the same way as in the case of the alloy 1101 casting, and its creep rupture strength was evaluated under the conditions of 982°C and 14 kgf/mm ^{2}.

[0069] The creep rupture time of the specimen collected from the alloy 1101 wheel was 1,800 hours as compared to 450 hours of the specimen collected from the USP 3,720,509 alloy wheel, demonstrating that the rupture time of the alloy 1101 wheel is more than 4 times longer than that of the above US patent alloy wheel.

Advantages of the Invention

[0070] According to the present invention, there can be obtained an Ni-base superalloy possessing high high-temperature strength and ductility no matter whether it is used for directionally solidified castings or for conventional castings. The gas turbines, blade cast from the Ni-base superalloy of the present invention by a directional solidification method are expected to realize a drastic improvement of thermal efficiency of the turbines with a low cost. Also, higher strength and use at higher temperatures can be realized with the centrifugal wheels for turbo chargers or microturbines which have been produced with the conventional castings and to which application of the directionally solidified castings has been difficult because of the configurational reason.

Claims

1. A high strength and high ductility Ni-base superalloy comprising, in percent (%) by weight, 0.06 to 0.3% of C, 0.01 to 0.05% of B, 0.2 to 3.0% of Hf, 10.2 to 25% of Co, 1 to 12% of Ta, 1.5 to 16% of Cr, 0 to 0.95% of Mo, 2 to 15% of W, 3.5 to 6.5% of Al, 0.5 to 9% of Re, 0.2 to 2% of Nb, 0 to 1% of V, 0 to 0.02% of Zr, 0 to 2% of at least one of platinum group elements, 0 to 2% of at least one of rare earth elements, 0 to 0.1% of at least one of alkaline earth metals and Si, 0 to 5% of at least one element selected from Fe, Ga and Ge, and the balance consisting of Ni and unavoidable impurities.

2. A high strength and high ductility Ni-base superalloy according to Claim 1 which contains, in percent (%) by weight, 1.1 to 3.0% of Hf.

3. A high strength and high ductility Ni-base superalloy produced by a conventional casting method and having a polycrystal texture, said superalloy comprising, in percent (%) by weight, 0.16 to 0.3% of C, 0.016 to 0.05% of B, 1.4 to 3.0% of Hf, 10.2 to 25% of Co, 1 to 4.9% of Ta, 1.5 to 8% of Cr, 0 to 0.95% of Mo, 7.2 to 15% of W, 3.5 to 6.5% of Al, 1.1 to 9% of Re, 0.2 to 2% of Nb, 0 to 1% of V, 0 to 0.02% of Zr, 0 to 2% of at least one of platinum group elements, 0 to 2% of at least one of rare earth elements, 0 to 0.1% of at least one of alkaline earth metals and Si, 0 to 5% of at least one element selected from Fe, Ga and Ge, and the balance consisting of Ni and unavoidable impurities.

4. A high strength and high ductility Ni-base superalloy according to Claim 3 which contains, in percent (%) by weight, 1.5 to 7% of Cr and 9 to 15% of W.

5. A high strength and high ductility Ni-base superalloy according to Claim 3 or 4 which contains, in percent (%) by weight, 1.5 to 7% of Cr and 11.2 to 15% of W.

6. A high strength and high ductility Ni-base superalloy according to any of Claims 3 to 5 which contains, in percent (%) by weight, 0.18 to 0.3% of C, 1.8 to 3.0% of Hf, 1.5 to 7% of Cr and 11.2 to 15% of W.

7. A high strength and high ductility Ni-base superalloy according to any of Claims 3 to 6 wherein the W/(W + Ta) ratio is 0.6 to 0.8.

8. A high strength and high ductility Ni-base superalloy produced by a directional solidification method and comprising, in percent (%) by weight, 0.06 to 0.3% of C, 0.01 to 0.05% of B, 1.4 to 3.0% of Hf, 10.2 to 25% of Co, 1 to 12% of Ta, 1.5 to 16% of Cr, 0 to 0.95% of Mo, 7.2 to 15% of W, 3.5 to 6.5% of Al, 1.1 to 9% of Re, 0.2 to 2% of Nb, 0 to 1% of V, 0 to 0.02% of Zr, 0 to 2% of at least one of platinum group elements, 0 to 2% of at least one of rare earth elements, 0 to 0.1% of at least one of alkaline earth metals and Si, 0 to 5% of at least one element selected from Fe, Ga and Ge, and the balance consisting of Ni and unavoidable impurities.

9. A high strength and high ductility Ni-base superalloy according to Claim 8 which contains, in percent (%) by weight, 1 to 6.5% of Ta and 9 to 15% of W.

10. A high strength and high ductility Ni-base superalloy according to Claim 8 or 9 which contains, in percent (%) by weight, 1 to 6.5% of Ta and 10.5 to 15% of W.

11. A high strength and high ductility Ni-base superalloy according to any of Claims 8 to 10 which contains, in percent (%) by weight, 1 to 4.9% of Ta and 11.2 to 15% of W.

12. A high strength and high ductility Ni-base superalloy according to any of Claims 8 to 11 wherein the W/(W + Ta) ratio is 0.6 to 0.8.

13. A high strength and high ductility Ni-base superalloy according to any of Claims 8 to 10 and 12 which contains, in percent (%) by weight, 1 to 6.5% of Ta and 10.5 to 15% of W, with the total content of Ta and W being 15 to 17%

and the W/(W + Ta) ratio being 0.6 to 0.8.

14. A high strength and high ductility Ni-base superalloy according to any of Claims 8 to 12 which contains, in percent (%) by weight, 1 to 4.9% of Ta and 11.2 to 15% of W, with the total content of Ta and W being 15 to 17% and the W/(W + Ta) ratio being 0.6 to 0.8.

15. A Ni-base superalloy castings having the composition defined in Claim 1.

16. The Ni-base superalloy castings according to Claim 15 produced by a directional solidification or a conventional casting method and having a single, columnar or polycrystal texture.

17. A master ingot for producing the Ni-base superalloy castings, said master ingot having the composition defined in Claim 1.

18. A centrifugal wheel for turbo chargers or microturbines, wherein said wheel is formed from the Ni-base superalloy having the composition defined in Claim 1.

19. The centrifugal wheel according to Claim 18 wherein a surface of a blade portion of the wheel is composed of fine grains, a portion extending from the blade portion toward a hub portion is composed of columnar grains oriented in a solidification direction from the blade portion toward the hub portion, and the hub portion is composed of coarse grains having a grain size of 5 mm or greater.

20. The centrifugal wheel according to Claim 19 which has a solidification form, in which a melt in contact with a solidification front is continuous all the way to a gate, at all of the surface of the blade portion of the wheel, in the whole region of the product.

21. A method of producing a centrifugal wheel comprising the steps of:

casting an Ni-base superalloy having the composition defined in Claim 1 into a centrifugal wheel for a turbo charger or
microturbine;
carrying out the casting in such a manner that the surface of the blade portion of the wheel will be composed of fine grains, the portion extending from the blade portion toward the hub portion will be composed of columnar grains oriented in the solidification direction from the blade portion toward the hub portion, and the hub portion will be composed of coarse grains having a grain size of 5 mm or greater; and then
subjecting the cast wheel to an HIP treatment for 2 hours or longer under the conditions of 1,185 to 1,285°C of temperature and 100 to 185 MPa of pressure; and then
subjecting it to a solution heat treatment.

22. A method of producing a centrifugal wheel according to claim 21 comprising the steps of:

casting an Ni-base superalloy having the composition defined in Claim 1 into a centrifugal wheel for a turbo charger or microturbine;
carrying out the casting in such a manner that the surface of the blade portion of the wheel will be composed of fine grains, the portion extending from the blade portion toward the hub portion will be composed of columnar grains oriented in the solidification direction from the blade portion toward the hub portion, and the hub portion will be composed of coarse grains having a grain size of 5 mm or greater, and that the cast product will have at its all portions a solidification form in which the melt in contact with the solidification front will be continuous all the way to the gate; and then
subjecting the cast wheel to an HIP treatment for 2 hours or longer under the conditions of 1,185 to 1,285°C of temperature and 100 to 185 MPa of pressure; and then subjecting it to a solution heat treatment.

23. An axial flow gas turbine blade cast from an Ni-base superalloy having the composition defined in Claim 1.

24. The axial flow gas turbine blade according to Claim 23 cast by the directional solidification method and having both a single crystal texture and a columnar grain texture.

FIG. 1


GRAIN BOUNDARY
DIRECTION OF SOLIDIFICATION
DIRECTION PERPENDICULAR TO SOLIDIFICATION

FIG. 2

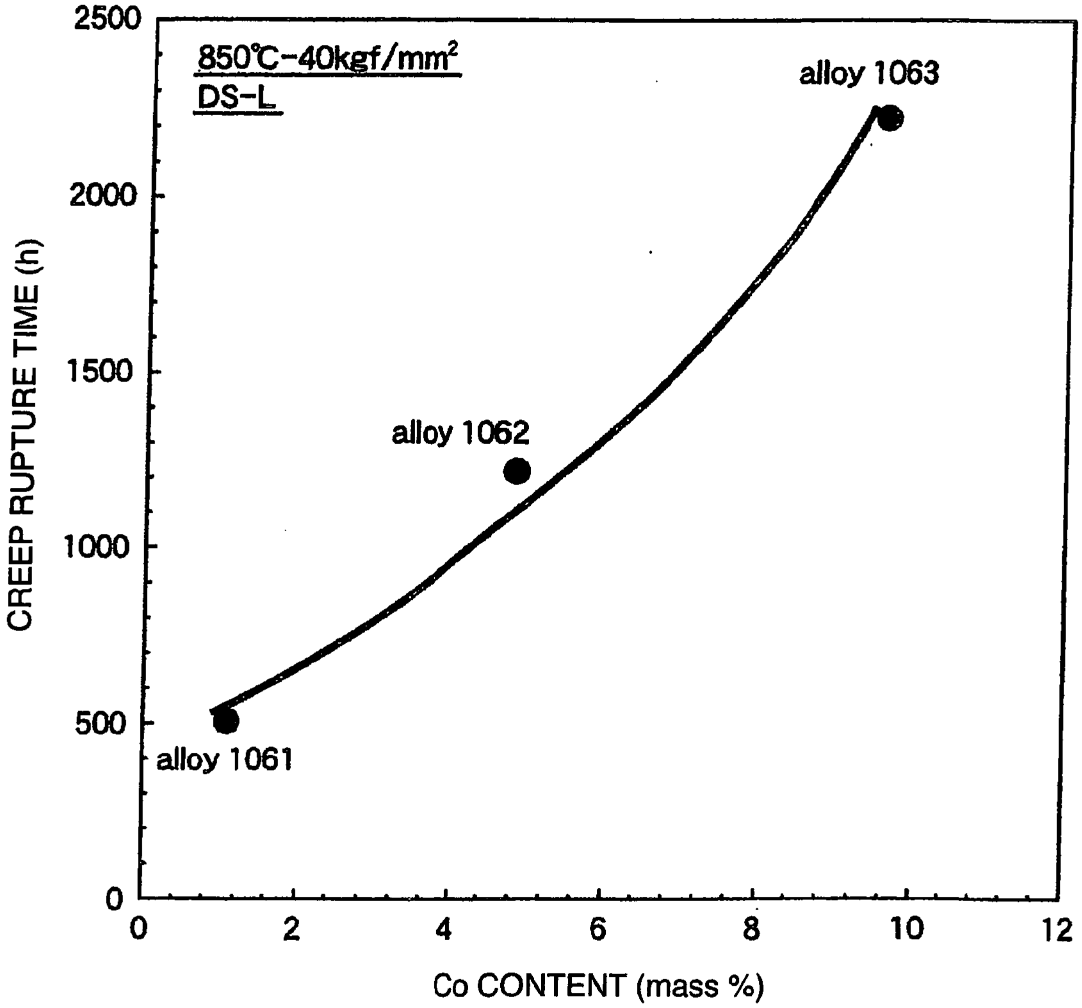

850℃-40kgf/mm²
DS-L
alloy 1063
alloy 1062
alloy 1061
CREEP RUPTURE TIME (h)
2500
2000
1500
1000
500
0
0
2
4
6
8
10
12
Co CONTENT (mass %)

FIG. 3

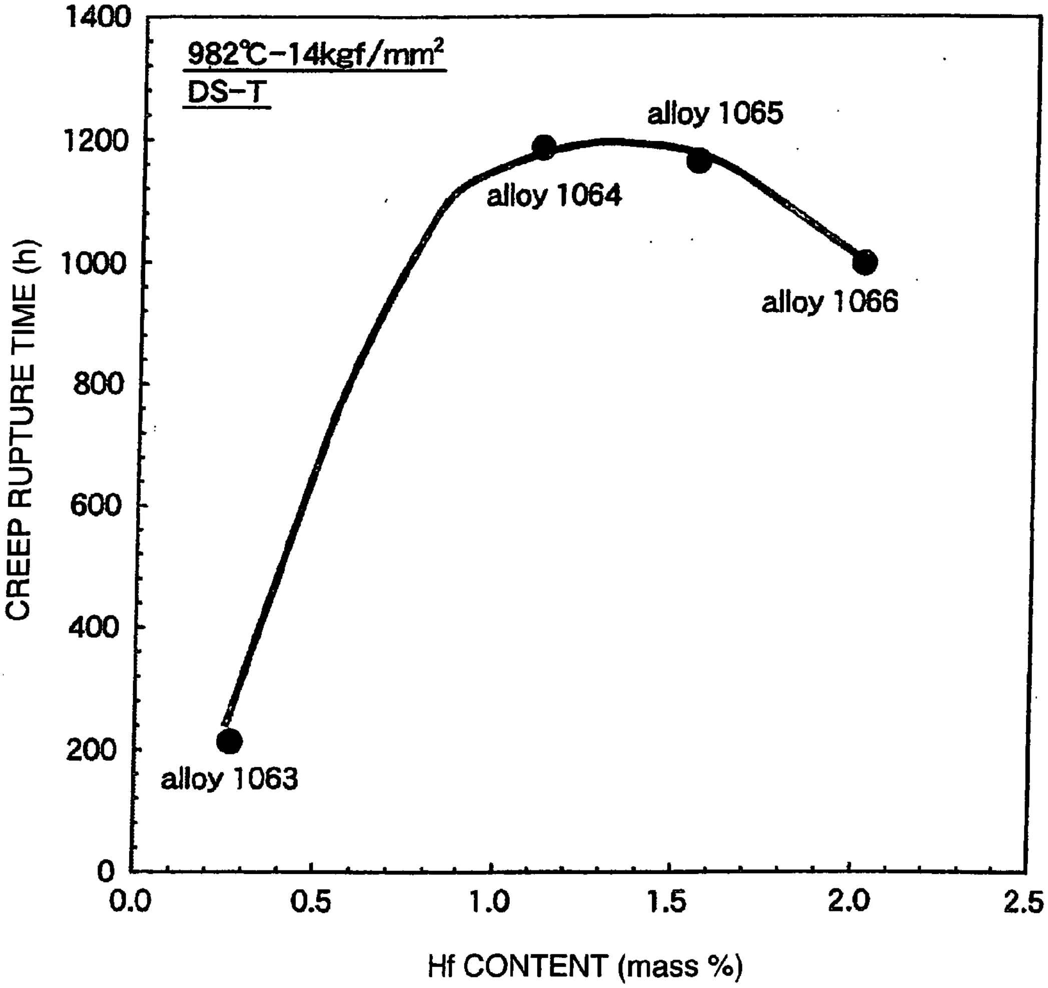

982℃-14kgf/mm²
DS-T
alloy 1063
alloy 1064
alloy 1065
alloy 1066
CREEP RUPTURE TIME (h)
0
200
400
600
800
1000
1200
1400
Hf CONTENT (mass %)
0.0
0.5
1.0
1.5
2.0
2.5

FIG. 4

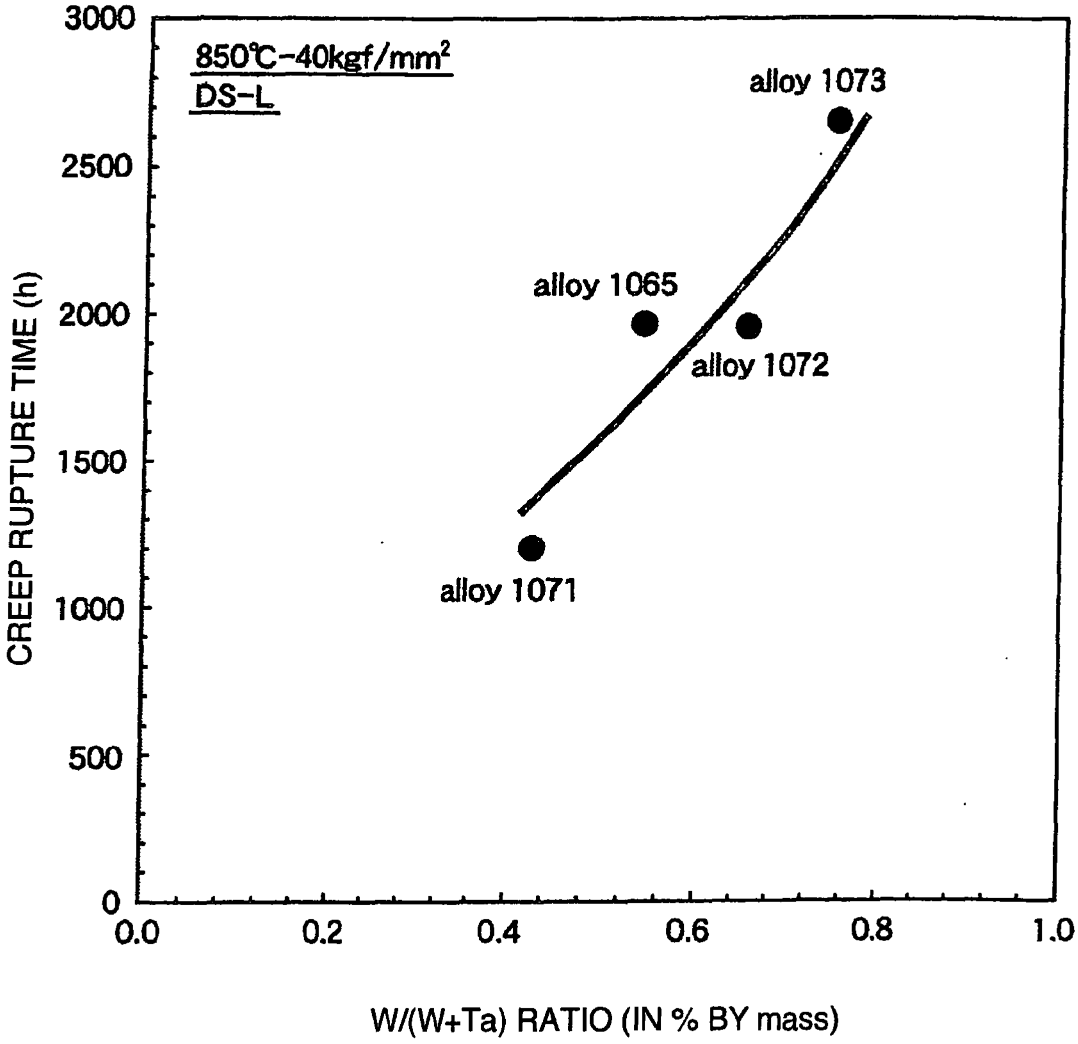

850℃-40kgf/mm²
DS-L
alloy 1073
alloy 1065
alloy 1072
alloy 1071
CREEP RUPTURE TIME (h)
3000
2500
2000
1500
1000
500
0
0.0
0.2
0.4
0.6
0.8
1.0
W/(W+Ta) RATIO (IN % BY mass)

FIG. 5

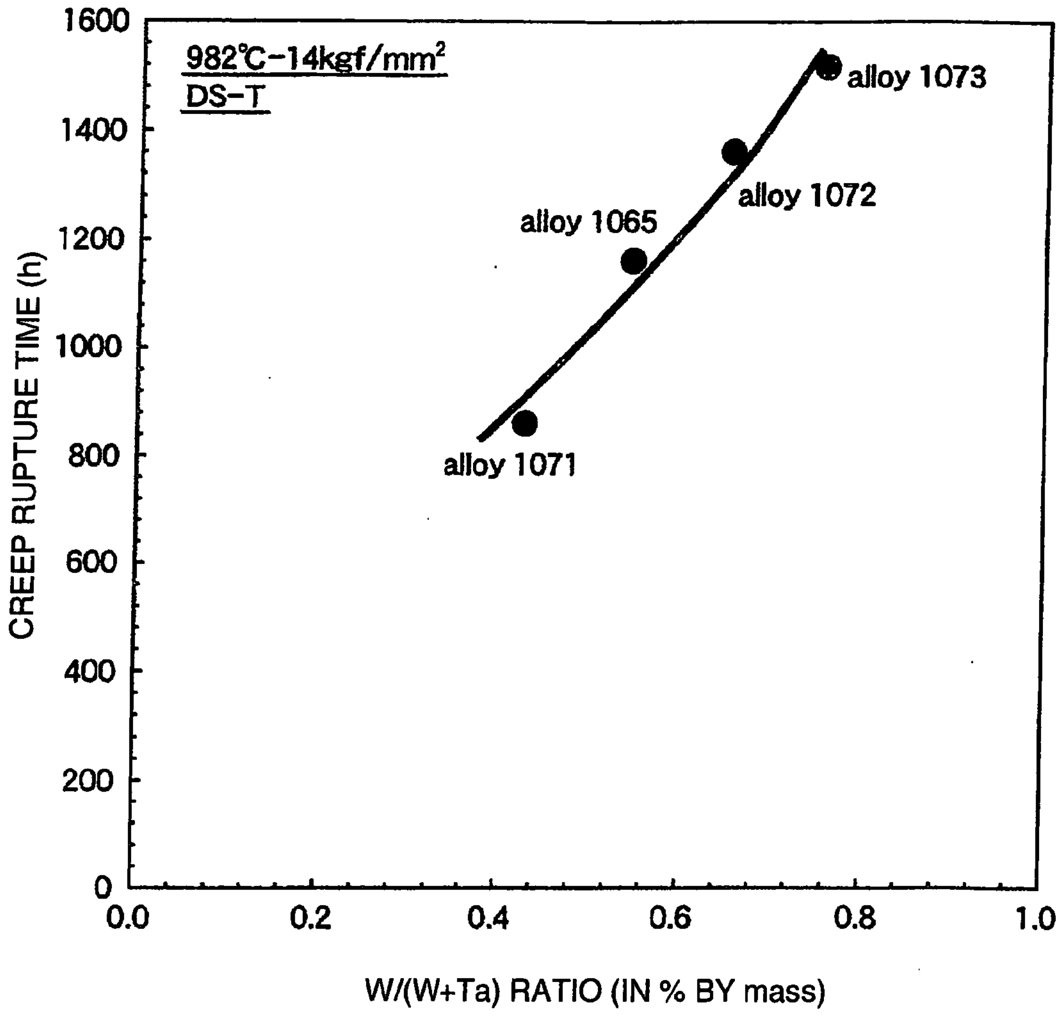

982℃-14kgf/mm^2
DS-T
CREEP RUPTURE TIME (h)
1600
1400
1200
1000
800
600
400
200
0
0.0
0.2
0.4
0.6
0.8
1.0
W/(W+Ta) RATIO (IN % BY mass)
alloy 1073
alloy 1072
alloy 1065
alloy 1071

FIG. 6

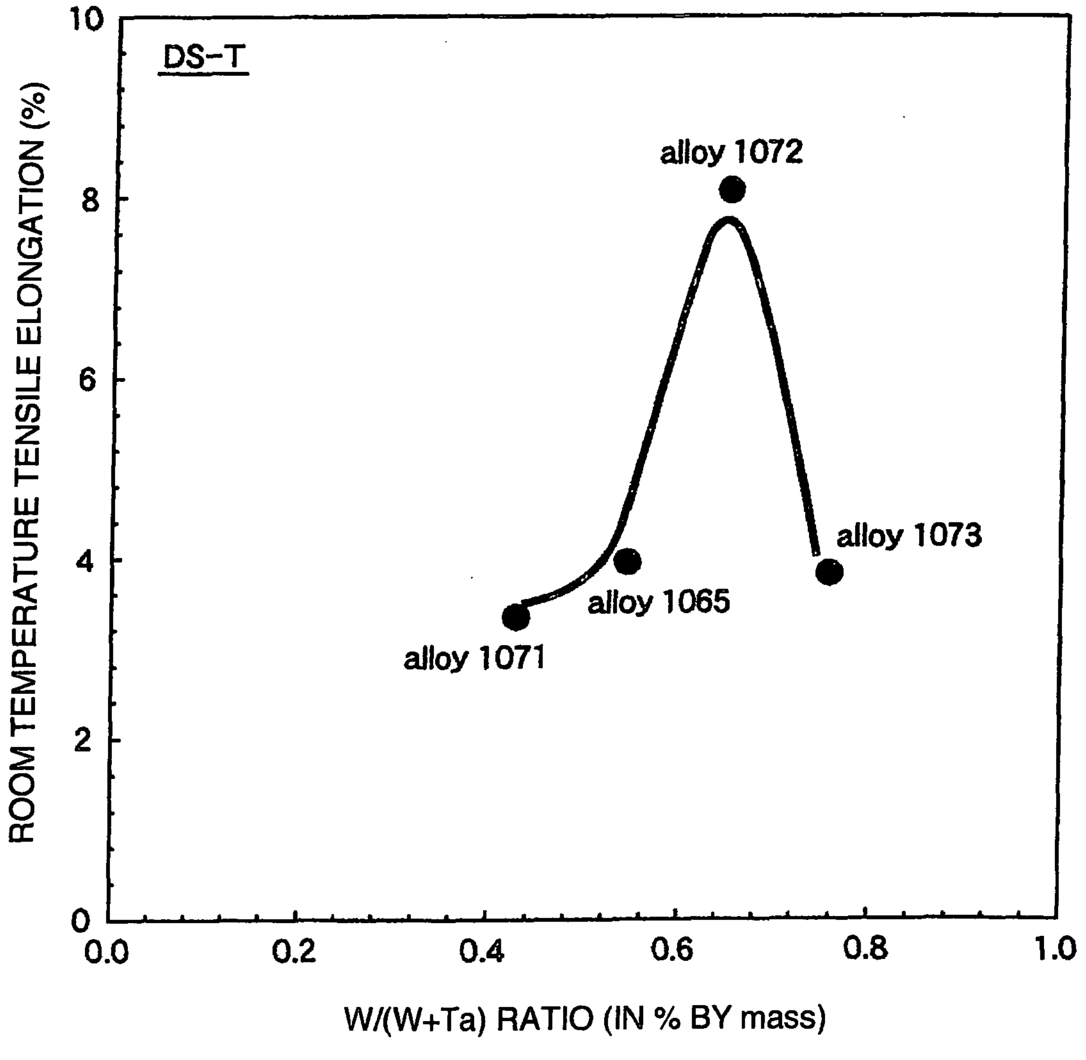

DS-T
ROOM TEMPERATURE TENSILE ELONGATION (%)
0
2
4
6
8
10
0.0
0.2
0.4
0.6
0.8
1.0
W/(W+Ta) RATIO (IN % BY mass)
alloy 1072
alloy 1073
alloy 1065
alloy 1071

FIG. 7

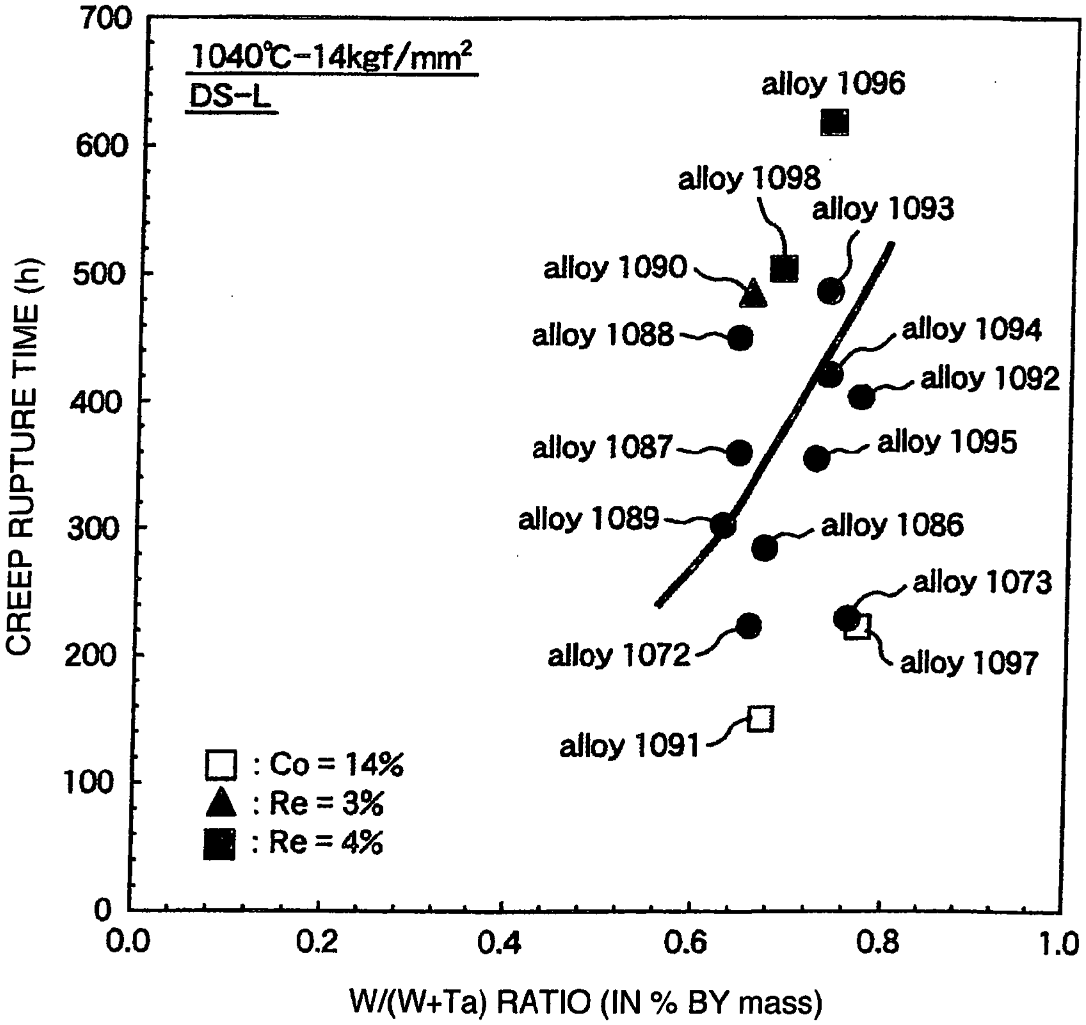

1040℃-14kgf/mm²
DS-L
alloy 1096
alloy 1098
alloy 1093
alloy 1090
alloy 1088
alloy 1094
alloy 1092
alloy 1087
alloy 1095
alloy 1089
alloy 1086
alloy 1073
alloy 1072
alloy 1097
alloy 1091
□ : Co = 14%
▲ : Re = 3%
■ : Re = 4%
CREEP RUPTURE TIME (h)
700
600
500
400
300
200
100
0
0.0
0.2
0.4
0.6
0.8
1.0
W/(W+Ta) RATIO (IN % BY mass)

FIG. 8

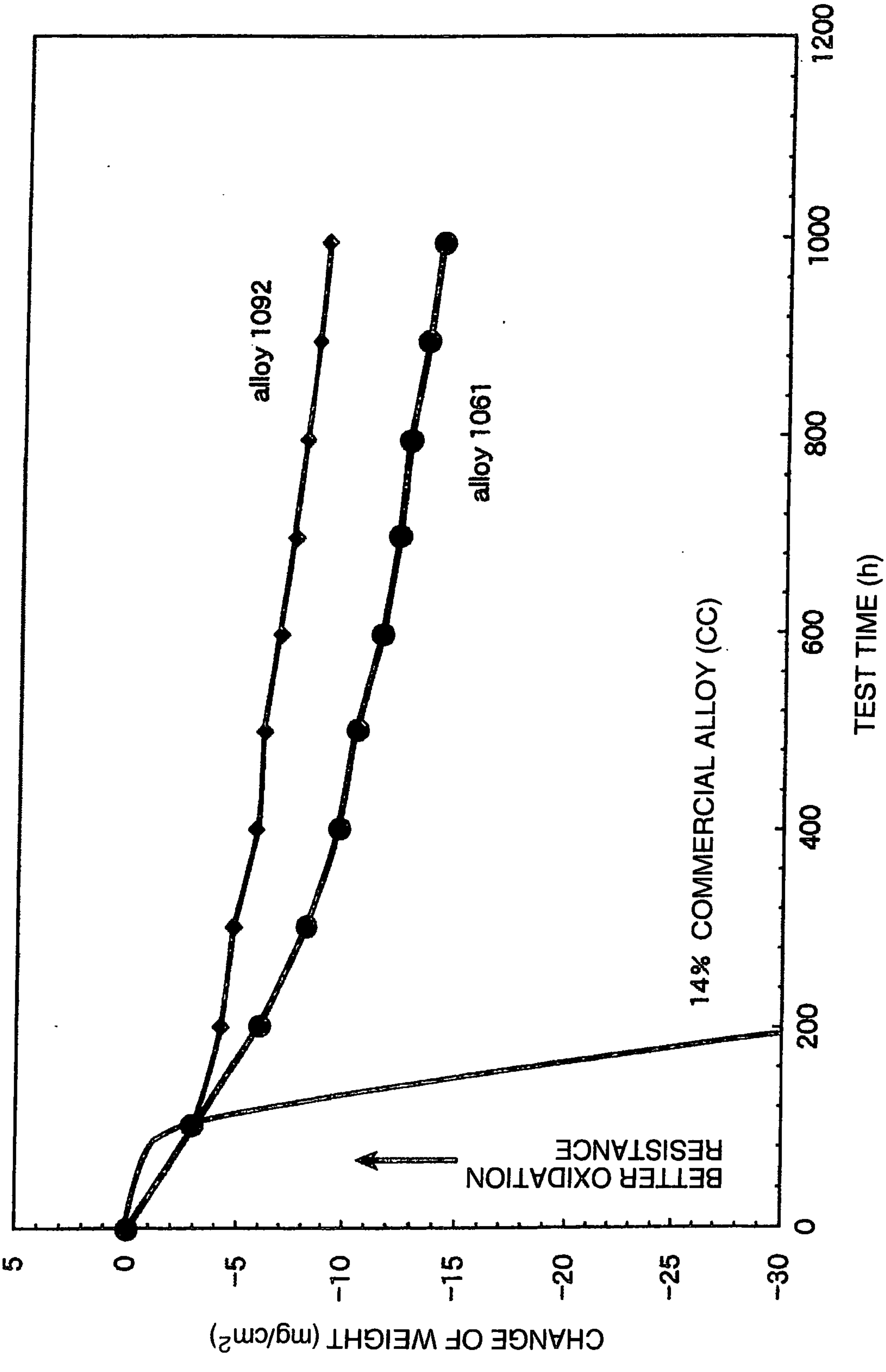

alloy 1092
alloy 1061
14% COMMERCIAL ALLOY (CC)
BETTER OXIDATION RESISTANCE
TEST TIME (h)
CHANGE OF WEIGHT (mg/cm²)
5
0
−5
−10
−15
−20
−25
−30
0
200
400
600
800
1000
1200

FIG. 9

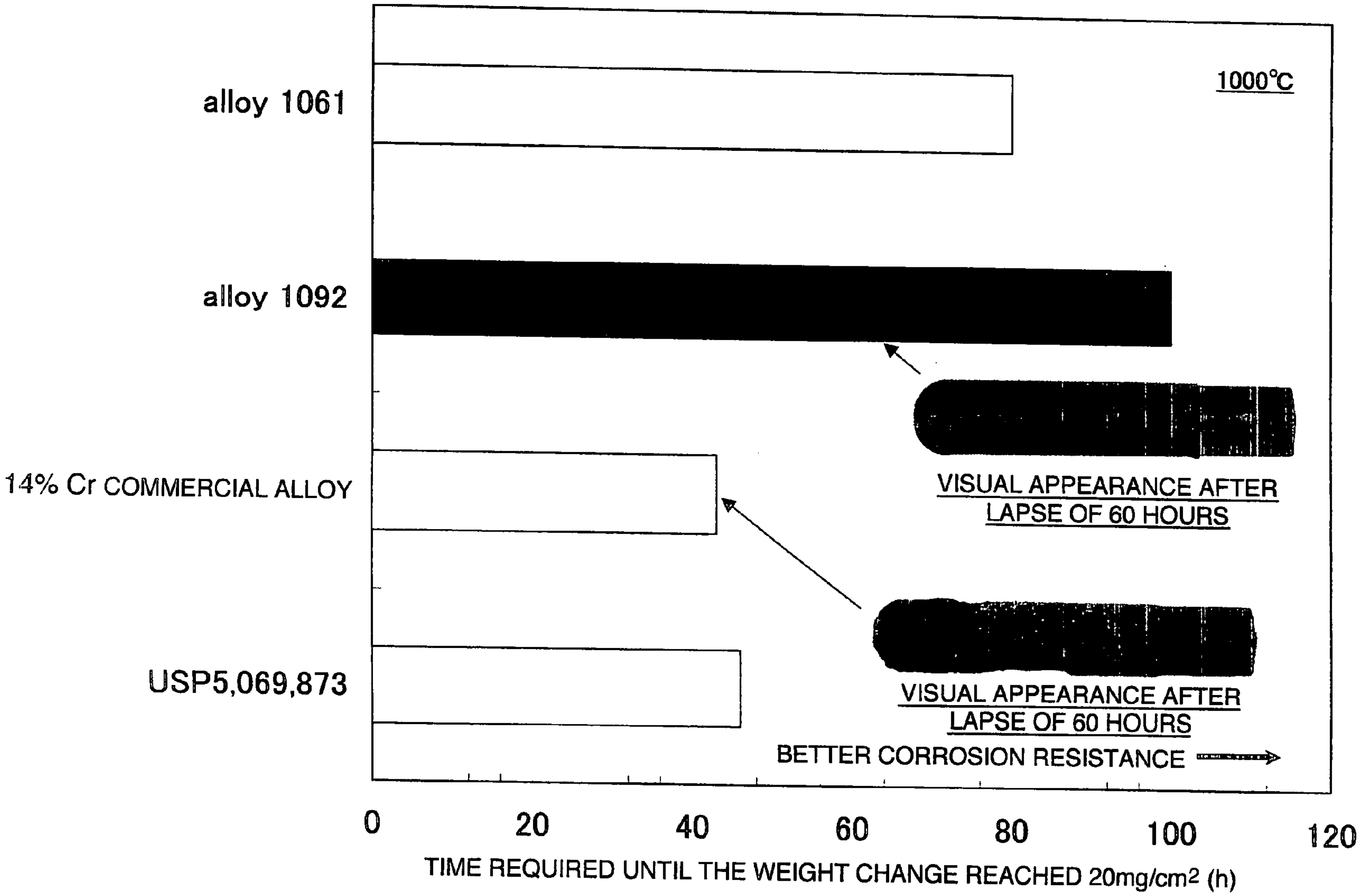

1000°C
alloy 1061
alloy 1092
14% Cr COMMERCIAL ALLOY
USP5,069,873
VISUAL APPEARANCE AFTER LAPSE OF 60 HOURS
VISUAL APPEARANCE AFTER LAPSE OF 60 HOURS
BETTER CORROSION RESISTANCE
0
20
40
60
80
100
120
TIME REQUIRED UNTIL THE WEIGHT CHANGE REACHED 20mg/cm2 (h)

FIG. 10

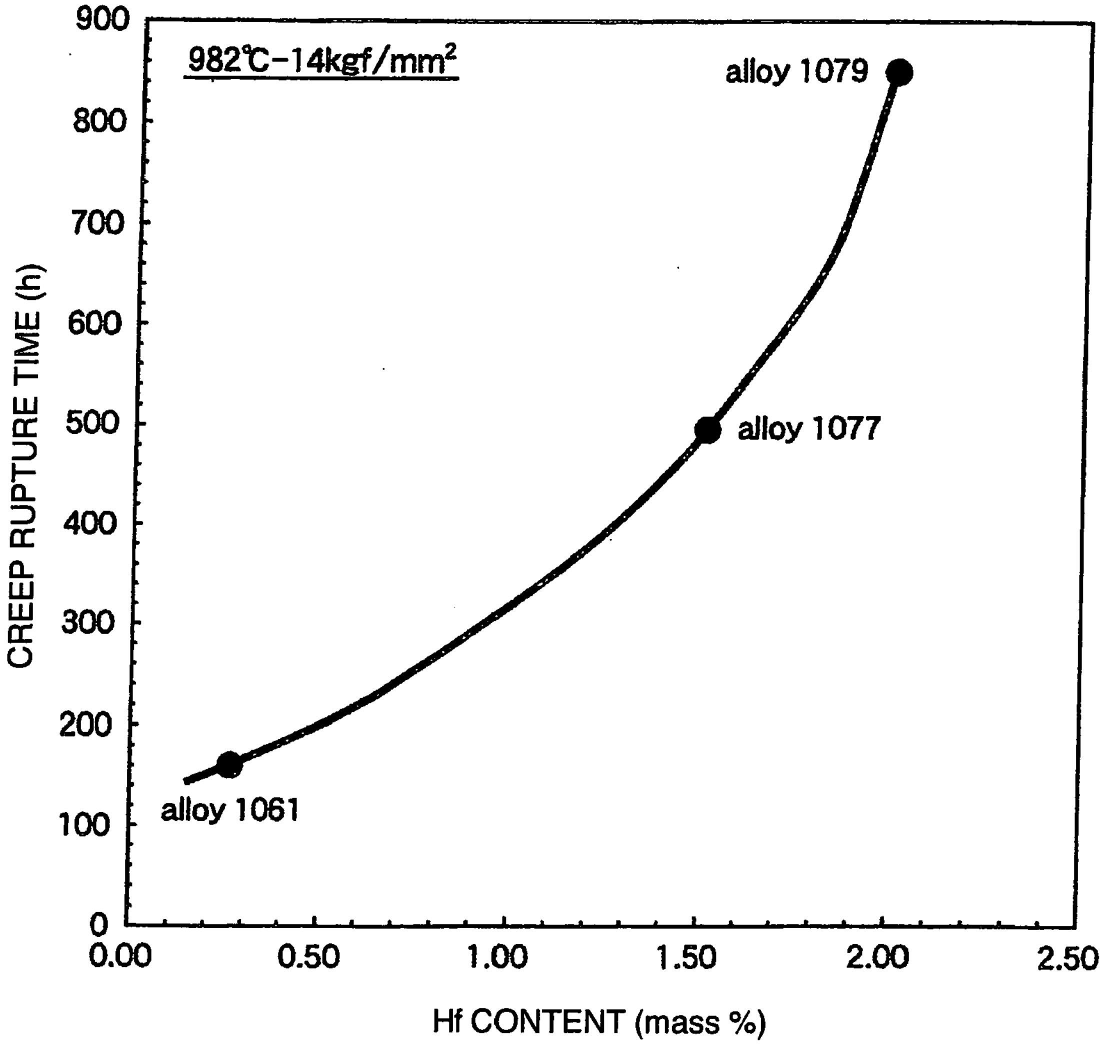

982℃-14kgf/mm²
alloy 1079
alloy 1077
alloy 1061
CREEP RUPTURE TIME (h)
900
800
700
600
500
400
300
200
100
0
0.00
0.50
1.00
1.50
2.00
2.50
Hf CONTENT (mass %)

FIG. 11

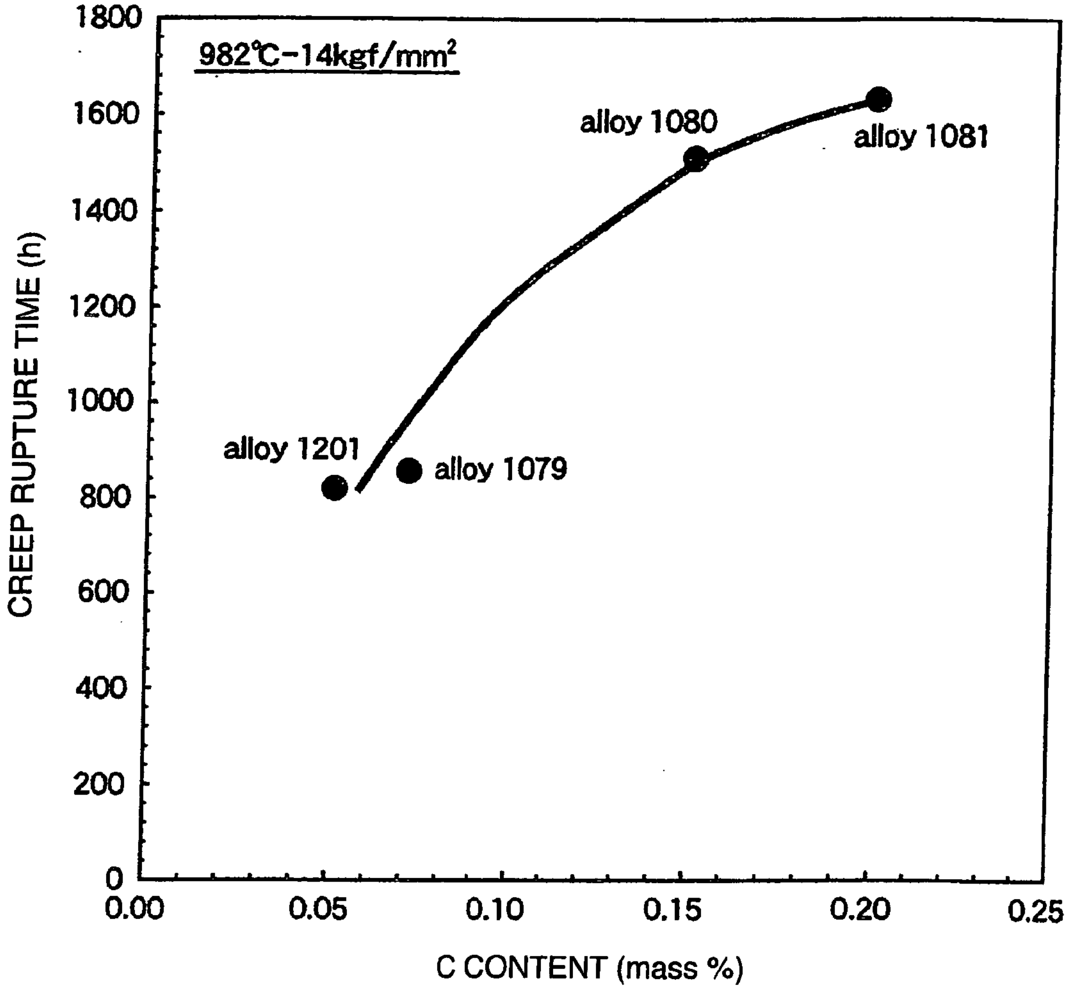

982℃-14kgf/mm²
CREEP RUPTURE TIME (h)
1800
1600
1400
1200
1000
800
600
400
200
0
0.00
0.05
0.10
0.15
0.20
0.25
C CONTENT (mass %)
alloy 1080
alloy 1081
alloy 1201
alloy 1079

FIG. 12

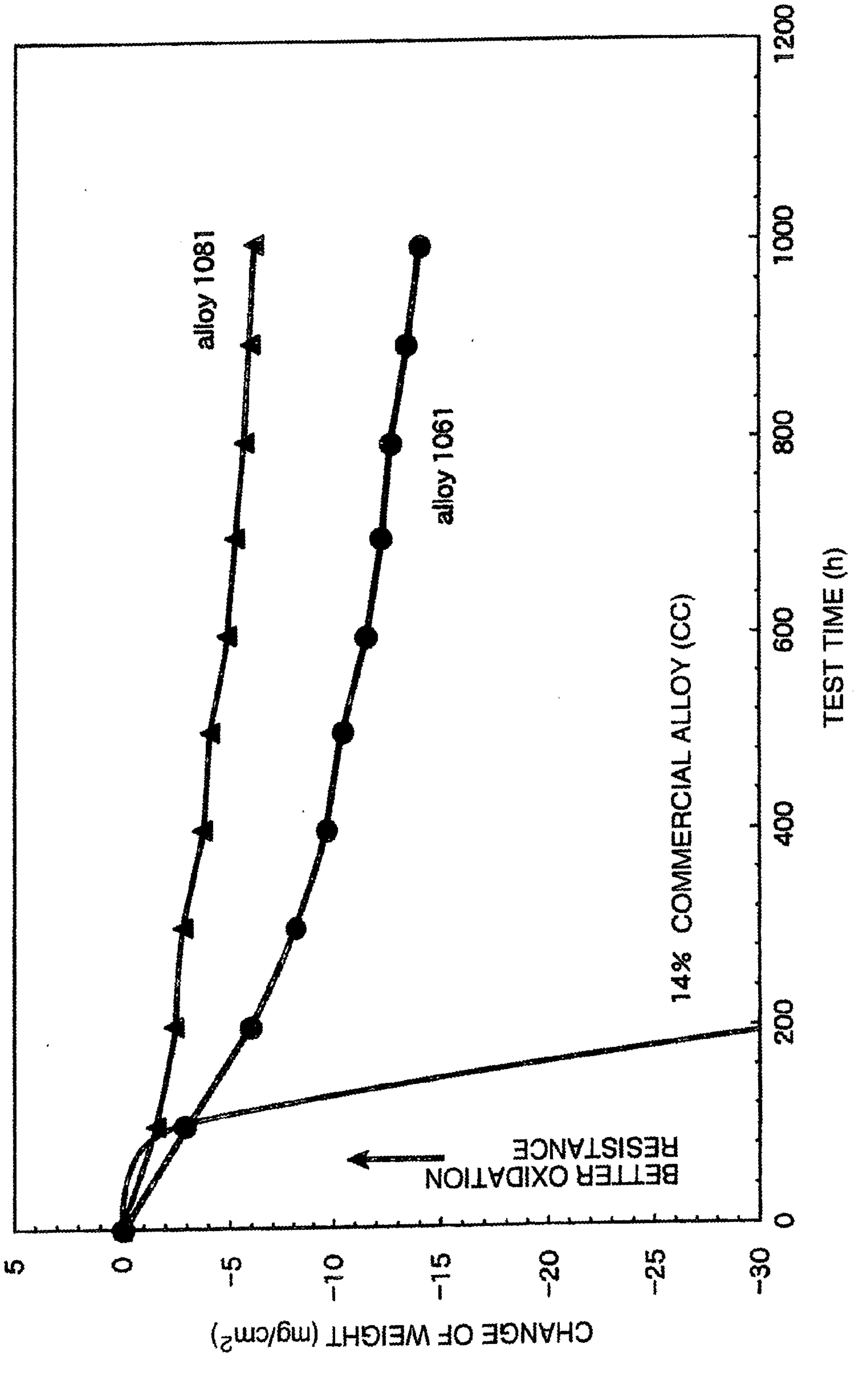

CHANGE OF WEIGHT (mg/cm^2)
5
0
−5
−10
−15
−20
−25
−30
TEST TIME (h)
0
200
400
600
800
1000
1200
alloy 1081
alloy 1061
14% COMMERCIAL ALLOY (CC)
BETTER OXIDATION RESISTANCE

FIG. 13

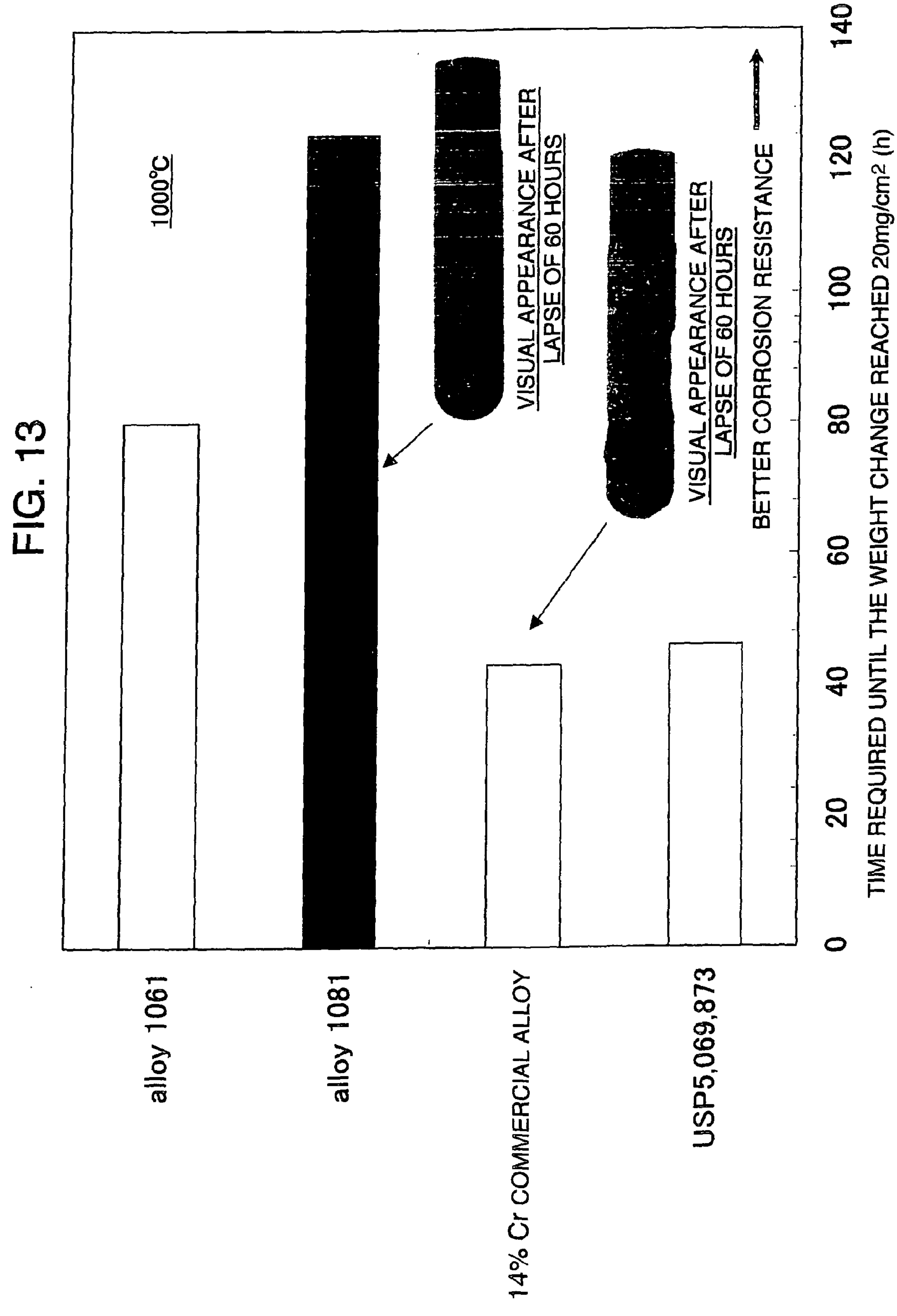

1000°C
alloy 1061
alloy 1081
14% Cr COMMERCIAL ALLOY
USP5,069,873
VISUAL APPEARANCE AFTER LAPSE OF 60 HOURS
VISUAL APPEARANCE AFTER LAPSE OF 60 HOURS
BETTER CORROSION RESISTANCE
0
20
40
60
80
100
120
140
TIME REQUIRED UNTIL THE WEIGHT CHANGE REACHED 20mg/cm2 (h)

FIG. 14

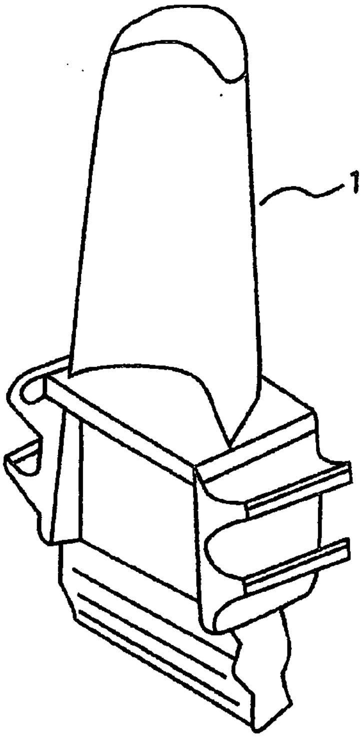


FIG. 15

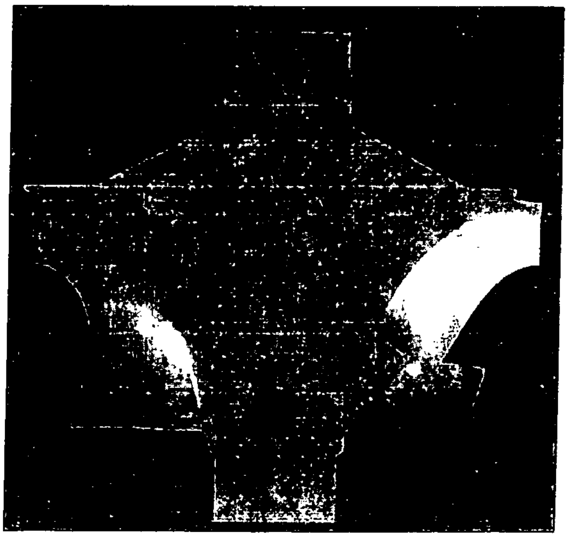


FIG. 16

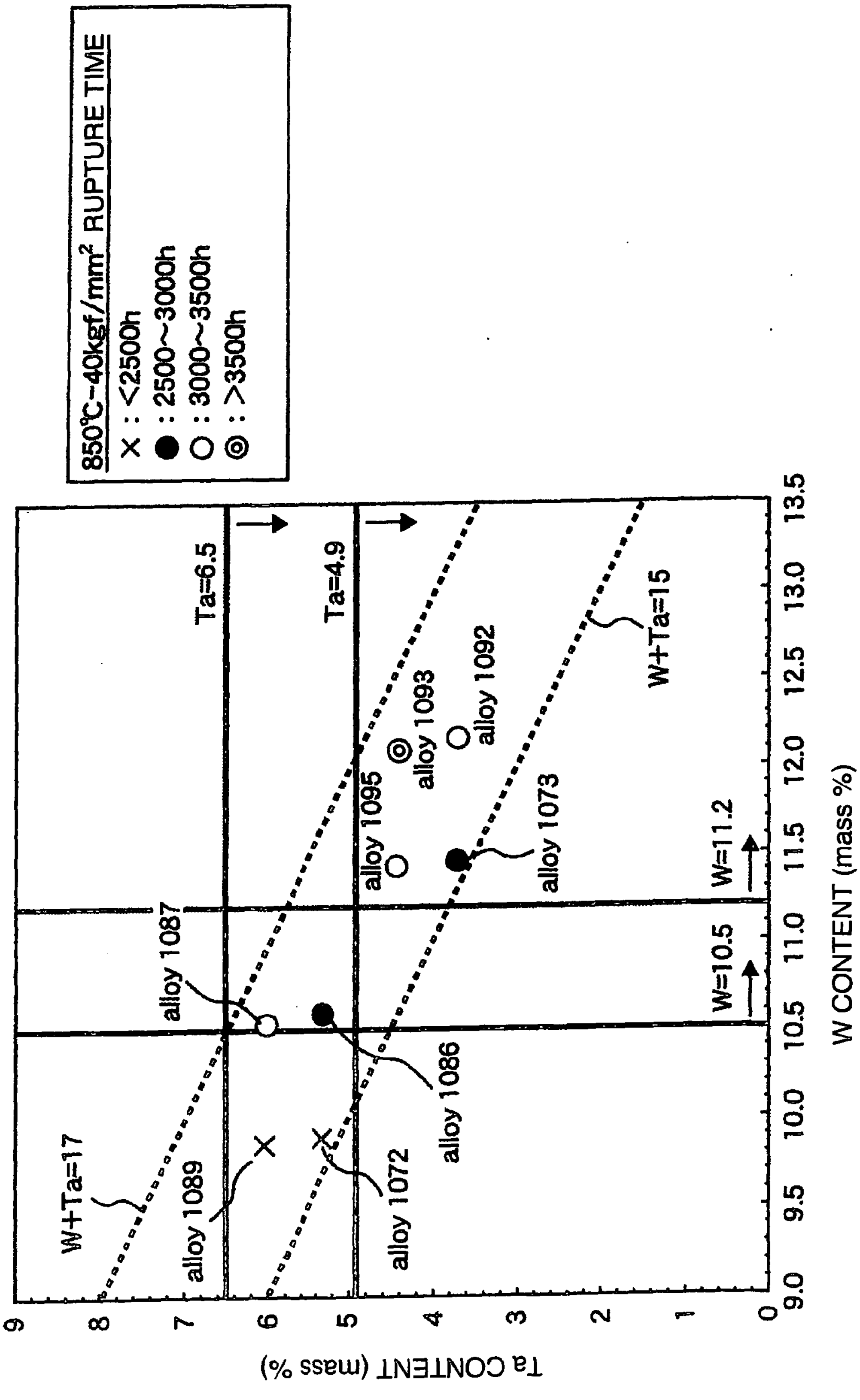
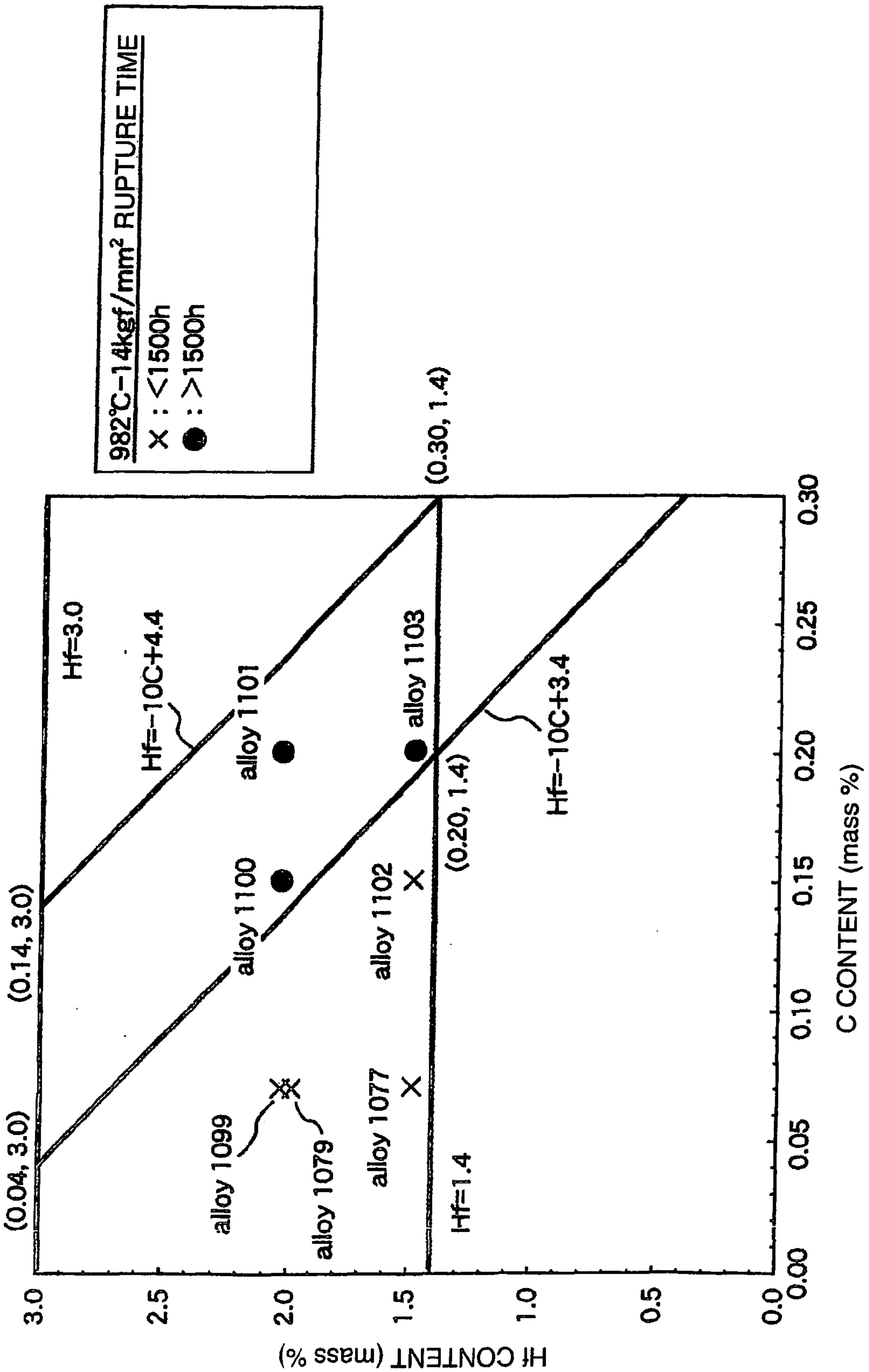

850°C-40kgf/mm² RUPTURE TIME
× : <2500h
● : 2500~3000h
○ : 3000~3500h
◎ : >3500h
Ta=6.5
Ta=4.9
W=10.5
W=11.2
W+Ta=17
W+Ta=15
alloy 1087
alloy 1089
alloy 1072
alloy 1086
alloy 1095
alloy 1073
alloy 1093
alloy 1092
W CONTENT (mass %)
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5
13.0
13.5
Ta CONTENT (mass %)
0
1
2
3
4
5
6
7
8
9

FIG. 17


982℃-14kgf/mm² RUPTURE TIME
× : <1500h
● : >1500h
(0.04, 3.0)
(0.14, 3.0)
(0.30, 1.4)
(0.20, 1.4)
Hf=3.0
Hf=1.4
Hf=-10C+4.4
Hf=-10C+3.4
alloy 1099
alloy 1079
alloy 1077
alloy 1100
alloy 1101
alloy 1102
alloy 1103
Hf CONTENT (mass %)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
C CONTENT (mass %)
0.00
0.05
0.10
0.15
0.20
0.25
0.30

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 02 5253

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	US 6 051 083 A (TAMAKI HIDEKI [JP] ET AL) 18 April 2000 (2000-04-18)	1,2, 15-17, 21-24	INV. C22C19/05
A	* claims 1-25; example 104; table 3 *	3-14, 18-20	
X	US 5 270 123 A (WALSTON WILLIAM S [US] ET AL) 14 December 1993 (1993-12-14)	1,2, 15-17, 21-24	
A	* claims 1-11; tables 1-3 *	3-14, 18-20	
X	EP 0 362 661 A1 (GEN ELECTRIC [US]) 11 April 1990 (1990-04-11)	1,2, 15-17, 21-24	
A	* claims 1-15; table VII *	3-14, 18-20	
A	US 6 096 141 A (KING WARREN TAN [US] ET AL) 1 August 2000 (2000-08-01) * claims 1-6 *	1-24	
			TECHNICAL FIELDS SEARCHED (IPC)
A	EP 0 560 296 A1 (HITACHI METALS LTD [JP]; HITACHI LTD [JP]) 15 September 1993 (1993-09-15) * claims 1-22; tables 1,2 *	1-24	C22C
A	US 5 783 318 A (BIONDO CHARLES M [US] ET AL) 21 July 1998 (1998-07-21) * claims 1-10; tables 1-5 *	1-24	
A	EP 1 057 899 A2 (GEN ELECTRIC [US]) 6 December 2000 (2000-12-06) * claims 1-14 *	1-24	
A	EP 0 663 462 A1 (GEN ELECTRIC [US]) 19 July 1995 (1995-07-19) * abstract *	1-24	
	-/--		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	9 February 2007	Catana, Cosmin

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

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 02 5253

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	EP 0 940 473 A1 (NAT RES INST METALS [JP]; KAWASAKI HEAVY IND LTD [JP]) 8 September 1999 (1999-09-08) * claims 1-12 * -----	1-24	
			TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	9 February 2007	Catana, Cosmin

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

2

EPO FORM 1503 03.82 (P04C01)

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

EP 06 02 5253

09-02-2007

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6051083 A	18-04-2000	DE 69701900 D1	15-06-2000
		DE 69701900 T2	07-12-2000
		EP 0789087 A1	13-08-1997
US 5270123 A	14-12-1993	US 5455120 A	03-10-1995
EP 0362661 A1	11-04-1990	AU 630623 B2	05-11-1992
		AU 4170089 A	05-04-1990
		DE 68921530 D1	13-04-1995
		DE 68921530 T2	26-10-1995
		ES 2070155 T3	01-06-1995
		GR 3015341 T3	30-06-1995
		IL 91793 A	31-07-1994
		JP 2153037 A	12-06-1990
		JP 3148211 B2	19-03-2001
		NO 893913 A	04-04-1990
US 6096141 A	01-08-2000	NONE	
EP 0560296 A1	15-09-1993	DE 69316251 D1	19-02-1998
		DE 69316251 T2	20-05-1998
US 5783318 A	21-07-1998	DE 69514809 D1	02-03-2000
		DE 69514809 T2	21-06-2000
		EP 0774015 A1	21-05-1997
		JP 10502416 T	03-03-1998
		WO 9535396 A1	28-12-1995
EP 1057899 A2	06-12-2000	US 6444057 B1	03-09-2002
EP 0663462 A1	19-07-1995	DE 69428511 D1	08-11-2001
		DE 69428511 T2	16-05-2002
		JP 3805396 B2	02-08-2006
		JP 7268520 A	17-10-1995
		US 5482789 A	09-01-1996
EP 0940473 A1	08-09-1999	JP 2905473 B2	14-06-1999
		JP 11246954 A	14-09-1999
		US 6224695 B1	01-05-2001

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 5069873 A **[0006] [0058] [0062] [0063]**
- US 6051083 A **[0006] [0043]**
- US 3720509 A **[0006] [0064] [0064] [0068] [0069]**