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(54) **Precipitation hardened Co-Ni based heat-resistant alloy and production method therefor**

(57) A precipitation hardened Co-Ni based heat-resistant alloy is composed of, all by weight, not more than 0.05% of C; not more than 0.5% of Si; not more than 1.0% of Mn; 25 to 45% of Ni; 13 to 22% of Cr; 10 to 18% of Mo or 10 to 18% of Mo + 1/2W; 0.1 to 5.0% of Nb; 0.1

to 5.0% of Fe; and further at least one kind of 0.007 to 0.10% of REM; 0.001 to 0.010% of B; 0.0007 to 0.010% of Mg and 0.001 to 0.20% of Zr; the balance of substantially Co and inevitable impurities, and Co₃Mo or Co₇Mo₆ is precipitated in boundaries between a fine twin structure and a parent phase.

Fig. 1



× 5000

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Description

BACKGROUND OF THE INVENTION

5 Field of the Invention

[0001] The present invention relates to a precipitation hardened Co-Ni based heat-resistant alloy and to a production method therefor, and more particularly, relates to a precipitation hardened Co-Ni based heat-resistant alloy in which Co_3Mo or Co_7Mo_6 is precipitated at boundaries between a fine twin structure and a parent phase. The structure is suitable for springs, bolts, etc., that are used in parts, such as engine exhaust systems and peripheral devices in gas turbines, which are exposed to high temperatures.

Related Art

15 **[0002]** Conventionally, heat-resistant parts which are used in parts, such as engine exhaust systems and peripheral devices in gas turbines, that are exposed to high temperatures, are manufactured by using Ni-based super heat-resistant alloys such as Inconel X-750 (Ni: 73.0 mass%, Cr: 15.0 mass%, Al: 0.8 mass%, Ti: 2.5 mass%, Fe: 6.8 mass%, Mn: 0.70 mass%, Si: 0.25 mass%, C: 0.04, Nb+Ta: 0.9 mass%) and Inconel 718 (Ni: 53.0 mass%, Cr: 18.6 mass%, Mo: 3.1 mass%, Al: 0.4 mass%, Ti: 0.9 mass%, Fe: 18.5 mass%, Mn: 0.20 mass%, Si: 0.18 mass%, C: 0.04 mass%, Nb+Ta: 5.0 mass%).

20 **[0003]** These Ni-based super-heat-resistant alloys are reinforced by precipitating γ' phase ($\text{Ni}_3(\text{Al}, \text{Ti}, \text{Nb})$) and γ'' phase (Ni_3Nb). However, when these alloys are used for long-periods at high temperatures at or above 600°C , the γ' phase and γ'' phase become coarse due to overaging, thereby causing a decrease in strength. Moreover, in parts such as springs and bolts on which stress is continuously applied, stress relaxation is large, and thereby there is failure to maintain initial performance originally required for the parts.

25 **[0004]** Therefore, the inventors of the present invention previously developed Co-Ni based heat-resistant alloys comprising, all by weight, not more than 0.05 mass% of C; not more than 0.5 mass% of Si; not more than 1.0 mass% of Mn; 25 to 45 mass% of Ni; 13 to less than 18 mass% of Cr; 7 to 20 mass% of Mo + 1/2W of at least one of Mo and W; 0.1 to 3.0 mass% of Ti; 0.1 to 5.0 mass% of Nb; 0.1 to 5.0 mass% of Fe; and the balance substantially of Co and inevitable impurities, the Co-Ni based heat-resistant alloy, as necessary, further comprising: 0.007 to 0.10 mass% of REM, further comprising, all by weight, at least one selected from the group consisting of 0.001 to 0.010 mass% of B; 0.0007 to 0.010 mass% of Mg; 0.001 to 0.20 mass% of Zr. The inventors also previously developed production methods for Co-Ni based heat-resistant alloys, comprising the steps of subjecting the alloy to a solid solution heat treatment at 1000 to 1200°C or a hot working at this temperature, then subjecting the alloy to a cold working or a warm working having a reduction ratio of not less than 40% and then subjecting the alloy to an aging heat treatment at 500 to 800°C for 0.1 to 50 hours. These inventions are disclosed in Japanese Unexamined Patent application (KOKAI) Publication No. 2002-97537.

30 **[0005]** In the Co-Ni based heat-resistant alloys, Cr which precipitates as a σ phase is at least needed, solute elements such as Mo, Fe, and Nb, which are segregated in stacking faults of extended dislocation to block dislocation movements, are increased to achieve high work hardening performance. These alloys have higher strengths at room temperature and can inhibit decrease in strength even after long-periods of use under high temperatures in comparison with conventional Ni-based super-heat-resistant alloys.

Summary of the Invention

45 **[0006]** Therefore, objects of the present invention are to provide a heat resistant alloy which exhibits higher strength than the above-mentioned Ni-based super-heat-resistant alloy and which can inhibit decrease in strength even after a long-period of use under high temperatures, and to provide a production method therefor.

50 **[0007]** In order to solve the above-mentioned problems, the inventors of the present invention have carried out various research and studies on the composition and aging heat treatment conditions of the Co-Ni based heat-resistant alloys which exhibit higher strengths than the above-mentioned Ni-based super-heat-resistant alloy, and can inhibit decrease in strength even after a long-period of use under high temperatures. As a result, the inventors found that when a Co-Ni based heat-resistant alloy is subjected to an aging heat treatment under conditions of applying stress or high temperature, a fine twin structure having an average grain size of several microns is formed, and Co_3Mo or Co_7Mo_6 with sizes from several micron to several tens of nanometers is precipitated in boundaries between the fine twin structure and a parent phase (refer to Fig. 1 and Fig. 2 showing structure photographs of Practical Example 22 of the present invention). The inventors also found that when the above-mentioned structure is formed, a heat-resistant alloy which has high strength and which can inhibit decrease in strength even after a long-period of use under high temperatures can be

obtained. The inventors also found that when Co-Ni based heat-resistant alloy is first subjected to a cold working or a warm working having a reduction ratio of not less than 40% after a solid solution heat treatment and is secondly subjected to an aging heat treatment, a dislocation with high density is formed in a matrix by the cold working or the warm working, whereby strength under high temperatures is improved by anchoring the dislocation by precipitates formed by an aging heat treatment after the solid solution heat treatment. Furthermore, a solute element such as Mo is segregated in stacking fault surfaces of dislocation, and the dislocation is anchored. Therefore, an improvement effect in the strength at room temperature and under high temperatures is obtained.

[0008] Moreover, the inventors found that in order to form a fine twin structure having an average grain size of several microns, and to form fine precipitates such as Co_3Mo or Co_7Mo_6 having grain size of from several microns to several tens of nanometers in boundaries between the fine twin structure and a parent phase, an aging heat treatment is performed in which heat-resistant alloy is heated in an adequate time to a temperature of 600 to 800°C in a condition of applying stress after the solid solution heat treatment. Alternatively, a working and an aging heat treatment is performed in which a heat-resistant alloy is first subjected to a cold working or a warm working having a reduction ratio of not less than 40% after a solid solution heat treatment and is secondly heated in an adequate time at a temperature of 600 to 800°C in a condition of applying stress. Alternatively, a working and an aging heat treatment is performed in which a heat-resistant alloy is first subjected to a cold working or a warm working having a reduction ratio of not less than 40% after a solid solution heat treatment and is secondly heated in an adequate time at a temperature of 800°C to 950°C.

[0009] The present invention has been made based on these findings. In the following explanation, "%" refers to mass%.

[0010] The present invention provides a precipitation hardened Co-Ni based heat-resistant alloy comprising, all by weight, not more than 0.05% of C; not more than 0.5% of Si; not more than 1.0% of Mn; 25 to 45% of Ni; 13 to 22% of Cr; 10 to 18% of Mo or 10 to 18% of Mo + 1/2W; 0.1 to 5.0% of Nb; 0.1 to 5.0% of Fe; if any 0.1 to 3.0% of Ti; at least one kind of 0.007 to 0.10% of REM; 0.001 to 0.010% of B; 0.0007 to 0.010% of Mg and 0.001 to 0.20% of Zr; the balance of Co and inevitable impurities; a fine twin structure; a parent phase; and Co_3Mo or Co_7Mo_6 is precipitated at boundaries of the fine twin structure and the parent phase.

[0011] In another aspect of the invention, the invention provides a production method for precipitation hardened Co-Ni based heat-resistant alloy, the method comprising the steps of: preparing an alloy comprising, all by weight, not more than 0.05% of C; not more than 0.5% of Si; not more than 1.0% of Mn; 25 to 45% of Ni; 13 to 22% of Cr; 10 to 18% of Mo or 10 to 18% of Mo + 1/2W; 0.1 to 5.0% of Nb; 0.1 to 5.0% of Fe; if any 0.1 to 3.0% of Ti; at least one kind of 0.007 to 0.10% of REM; 0.001 to 0.010% of B; 0.0007 to 0.010% of Mg and 0.001 to 0.20% of Zr; the balance of Co and inevitable impurities; subjecting the alloy to a solid solution heat treatment; and subjecting the alloy to an aging heat treatment at 600 to 800°C for 0.5 to 16 hours in a condition of applying stress, thereby forming a fine twin structure in a parent phase, and precipitating Co_3Mo or Co_7Mo_6 at a boundary of the fine twin structure and the parent phase.

[0012] Moreover, in another aspect of the invention, the invention provides a production method for precipitation hardened Co-Ni based heat-resistant alloy, the method comprising the steps of: preparing an alloy comprising, all by weight, not more than 0.05% of C; not more than 0.5% of Si; not more than 1.0% of Mn; 25 to 45% of Ni; 13 to 22% of Cr; 10 to 18% of Mo or 10 to 18% of Mo + 1/2W; 0.1 to 5.0% of Nb; 0.1 to 5.0% of Fe; if any 0.1 to 3.0% of Ti; at least one kind of 0.007 to 0.10% of REM; 0.001 to 0.010% of B; 0.0007 to 0.010% of Mg and 0.001 to 0.20% of Zr; the balance of Co and inevitable impurities; subjecting the alloy to a solid solution heat treatment; subjecting the alloy to a cold working or a warm working having a reduction ratio of not less than 40%; and subjecting the alloy to an aging heat treatment at 600 to 800°C for 0.5 to 16 hours in a condition of applying stress, thereby forming a fine twin structure in a parent phase, and precipitating Co_3Mo or Co_7Mo_6 at a boundary of the fine twin structure and the parent phase.

[0013] Furthermore, in another aspect of the invention, the invention provides a production method for precipitation hardened Co-Ni based heat-resistant alloy, the method comprising the steps of: preparing an alloy comprising, all by weight, not more than 0.05% of C; not more than 0.5% of Si; not more than 1.0% of Mn; 25 to 45% of Ni; 13 to 22% of Cr; 10 to 18% of Mo or 10 to 18% of Mo + 1/2W; 0.1 to 5.0% of Nb; 0.1 to 5.0% of Fe; if any 0.1 to 3.0% of Ti; at least one kind of 0.007 to 0.10% of REM; 0.001 to 0.010% of B; 0.0007 to 0.010% of Mg and 0.001 to 0.20% of Zr; the balance of Co and inevitable impurities; subjecting the alloy to a solid solution heat treatment; subjecting the alloy to a cold working or a warm working having a reduction ratio of not less than 40%; and subjecting the alloy to an aging heat treatment at 800°C to 950°C for 0.5 to 16 hours, thereby forming a fine twin structure in a parent phase, and precipitating Co_3Mo or Co_7Mo_6 at a boundary of the fine twin structure and the parent phase.

[0014] In the precipitation hardened Co-Ni based heat-resistant alloy of the present invention, fine precipitates are formed at boundaries between the fine twin structure and a parent phase. The precipitates are not grown to be coarse at high temperatures of about 700°C, an effect on anchoring dislocation is performed even at high temperatures of not less than 700°C due to interaction between the precipitates and the dislocation. The precipitates are formed in grain boundaries of a fine twin structure having average grain size of several microns. Therefore, the precipitates suppress grain boundary sliding as an obstacle when the grain boundary moves at high temperatures of not less than 700°C, and

prevents coarsening of the grains. Accordingly, high strength, such as creep strength, is excellent.

[0015] Moreover, in the production method of the precipitation hardened Co-Ni based heat-resistant alloy of the present invention, the heat-resistant alloy is subjected to an aging heat treatment for 0.5 to 16 hours at a temperature of 600 to 800°C in a condition of applying stress after a solid solution heat treatment by heating at 1000 to 1200°C. Alternatively, the heat-resistant alloy is first subjected to a cold working or a warm working having a reduction ratio of not less than 40% after the solid solution heat treatment and is secondly subjected to an aging heat treatment for 0.5 to 16 hours at a temperature of 600 to 800°C in a condition of applying stress. Alternatively, the heat-resistant alloy is first subjected to a cold working or a warm working having a reduction ratio of not less than 40% after the solid solution heat treatment and secondly to an aging heat treatment by heating for 0.5 to 16 hours at temperature of 800°C to 950°C. Therefore, the fine twin structure can be formed and at least one kind of Co_3Mo and Co_7Mo_6 can be precipitated in boundaries between the fine twin structure and a parent phase.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016]

Fig. 1 is a scanning electron micrograph of drawing substitution showing a structure magnified 5000 times of Practical Example No. 22 of the present invention.

Fig. 2 is a scanning electron micrograph of drawing substitution showing a structure magnified 2000 times of Practical Example No. 22 of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0017] Next, the following description will discuss the reasons for the above-mentioned limitations to the composition in the precipitation hardened Co-Ni based heat-resistant alloy and the production method of the present invention.

C: Not more than 0.05%

[0018] Carbon C is bound to Nb and Ti to form carbides to prevent grains from becoming coarse at the time of a solid solution heat treatment, and also to strengthen the grain boundary; thus, this element is contained for these purposes. In order to obtain these effects, the content must be not less than 0.005%. However, since a content exceeding 0.05%, more specifically, 0.03%, would cause decrease in the toughness and corrosion resistance, and would also form a carbide with a dislocation anchoring element such as Mo, thereby resulting in interference with the dislocation anchoring, the content must not be more than 0.05%. The preferable range is 0.005 to 0.03%.

Si: Not more than 0.5%

[0019] Since Si is effectively used as a deoxidizer, this element is contained for this purpose. However, since a content exceeding 0.5%, more specifically, 0.3%, would cause decrease toughness, the content is not more than 0.5%. The preferable range is not more than 0.3%.

Mn: Not more than 1.0%

[0020] Since Mn is effectively used as a deoxidizer, and reduces stacking fault energy to improve the work hardening performance, this element is contained for this purpose. However, since a content exceeding 1.0%, more specifically, 0.7%, would cause decrease in corrosion resistance, the content must not be more than 1.0%. The preferable range is not more than 0.7%.

Ni: 25 to 45%

[0021] Since Ni is an element that is used for stabilizing austenite serving as a matrix and improves heat resistance and corrosion resistance of the alloy, this element is contained for these purposes. In order to obtain these effects, the content must not be less than 25%, more preferably, 27%. However, since a content exceeding 45%, would cause decrease in work hardening performance, the content must be 25 to 45%. The preferable range is 27 to 45%.

Cr: 13% to less than 22%

[0022] Since Cr is an element that is used for improving the heat resistance and corrosion resistance, this element is contained for these purposes. In order to obtain these effects, the content must not be less than 13%, more preferably, 16%. However, since a content exceeding 22%, more specifically, 21%, tends to cause precipitation of a σ phase, the content must be in a range of 13 to 22%. The preferable range is 16 to 21%.

Mo + 1/2W: 10 to 18%

[0023] Since Mo and W are solid solution-treated into the matrix and strengthen the matrix to improve the work hardening performance, these elements are contained for these purposes. In order to obtain these effects, the content must not be less than 10%, more preferably, 11%, and preferably the Mo content must not be less than 8.0% in the case of containing Mo and W. However, since when the total amount of the content of Mo and 1/2 of the content of W exceeds 18%, precipitation of a σ phase tends to occur, the content must be in a range of 10 to 18%. The preferable range is 11 to 18%.

Nb: 0.1 to 5.0%

[0024] Nb is bound to C to form carbides to prevent grains from becoming coarse in a solid solution heat treatment and to strengthen the grain boundary, and also solid solution-treated in the matrix to strengthen the matrix, thereby improving the work hardening performance. Thus, this element is contained for these purposes. In order to obtain these effects, the content must not be less than 0.1%, more preferably, 0.8%. However, since the content exceeding 5.0%, more specifically, 3.0%, would cause precipitation of a σ phase (Ni_3Nb) resulting in decrease in workability and toughness, the content must be in a range of 0.1 to 5.0%. The preferable range is 0.8 to 3.0%.

Fe: 0.1 to 5.0%

[0025] Since Fe is solid solution-treated in the matrix to strengthen the matrix, this element is contained for this purpose. In order to obtain this effect, the content must not be less than 0.1%, and more preferably, 0.5%. However, since a content exceeding 5.0%, more specifically, 4.8%, causes decrease in oxidation resistance property, the content must be in a range of 0.1 to 5.0%. The preferable range is 0.5 to 4.8%.

[0026] The application of Mo, Nb, and Fe in a combined manner makes it possible to greatly increase the solid solution strength and work hardening of the matrix, which greatly enhances the maximum tensile strength obtained at room temperature and at high temperatures, and exerts an effect of shifting the temperature having a maximum of the tensile strength at a high temperature to the high temperature side, in comparison with the application of Mo and Nb or Mo and Fe in a combined manner.

Ti: 0.1 to 3.0%

[0027] Since Ti improves strength, this element is contained for this purpose. In order to obtain this effect, the content must not be less than 0.1%, more preferably, 0.5%. However, since a content exceeding 3.0%, more specifically, 2.5%, would cause precipitation of an η phase (Ni_3Ti) resulting in decrease in workability and toughness, the content must be in a range of 0.1 to 3.0%. The preferable range is 0.5 to 2.5%.

REM: 0.007 to 0.10%

[0028] Since REM, which is at least one rare-earth elements such as Y, Ce, and misch metal, improves the hot workability and oxidation resistance property, this is contained for these purposes. In order to obtain these effects, the content must not be less than 0.007%, more preferably, 0.01%. However, since a content exceeding 0.10%, more specifically, 0.04%, causes decrease in hot workability and oxidation resistance property in an inverse manner, the content must be in a range of 0.007 to 0.10%. The preferable range is 0.01 to 0.04%.

B: 0.001 to 0.010%, Mg: 0.0007 to 0.010%, Zr: 0.001 to 0.20%.

[0029] Since B, Mg, and Zr improve the hot workability and strengthen the grain boundary, these elements are contained for these purposes. In order to obtain these effects, B must be 0.001%, more preferably, 0.002%, Mg must be 0.0007%, more preferably, 0.001%, and Zr must be 0.001%, more preferably, 0.01%. However, since B exceeding 0.010%, more specifically, 0.006%, Mg exceeding 0.010%, more specifically, 0.004% and Zr exceeding 0.20%, more specifically 0.05%, would cause decrease in hot workability and oxidation resistance property, the ranges of the contents must be respectively in the above-mentioned ranges. More preferably, B is in a range of 0.002 to 0.006%, Mg is in a range of 0.001 to 0.004%, and Zr is in a range of 0.01 to 0.05%.

Co: Balance

[0030] Co, which has a close-packed hexagonal lattice structure, is allowed to contain Ni so as to have a face-centered cubic lattice structure, that is, austenite, thereby exerting a high work hardening performance.

[0031] The precipitation hardened Co-Ni based heat-resistant alloy of the present invention comprises the above-mentioned composition, and has a structure in which Co_3Mo or Co_7Mo_6 is precipitated in boundaries between a fine twin structure and a parent phase.

[0032] Next, the following description will discuss the production method of the precipitation hardened Co-Ni based heat-resistant alloy of the present invention. In the production method of the precipitation hardened Co-Ni based heat-resistant alloy of the present invention, a fine twin structure having average grain size of several microns is formed in a precipitation hardened Co-Ni based heat-resistant alloy having the above-mentioned composition, Co_3Mo or Co_7Mo_6 of sizes from several microns to several tens of nanometers is precipitated in boundaries between the fine twin structure and a parent phase, and thereby a heat-resistant alloy which has high strength and which can inhibit decrease in strength even after a long-period of use under high temperatures can be obtained.

[0033] Therefore, the production method of the precipitation hardened Co-Ni based heat-resistant alloy of the present invention is characterized in that the above-mentioned Co-Ni based heat-resistant alloy is first subjected to a solid solution heat treatment by heating to 1000 to 1200°C, etc., and secondly to an aging heat treatment by heating for 0.5 to 16 hours at temperature of 600 to 800°C in a condition of applying stress. Furthermore, another production method of the precipitation hardened Co-Ni based heat-resistant alloy of the present invention is characterized in that the above-mentioned Co-Ni based heat-resistant alloy is first subjected to a solid solution heat treatment, secondly to a cold working or a warm working having a reduction ratio of not less than 40%, and thirdly to an aging heat treatment by heating for 0.5 to 16 hours to a temperature of 600 to 800°C in a condition of applying stress. Moreover, another production method of the precipitation hardened Co-Ni based heat-resistant alloy of the present invention is charac-

terized in that the above-mentioned Co-Ni based heat-resistant alloy is first subjected to a solid solution heat treatment, secondly to a cold working or a warm working having a reduction ratio of not less than 40%, and thirdly to an aging heat treatment by heating for 0.5 to 16 hours to a temperature of 800°C to 950°C in an unloaded condition.

5 [0034] In the production method of the precipitation hardened Co-Ni based heat-resistant alloy of the present invention, the solid solution heat treatment is performed in order to make the structure uniform and to lower the hardness to facilitate working. Therefore, the solid solution heat treatment is preferably performed by heating to 1000 to 1200°C. A temperature lower than 1000°C fails to provide a sufficiently uniform structure and also fails to lower the hardness, thereby causing difficulty in working. Furthermore, a temperature lower than 1000°C might cause precipitation of a compound such as Mo that exerts an anchoring effect on dislocations, and a subsequent reduction in the age hardening property. A temperature exceeding 1200°C makes crystal grains coarse, resulting in decrease in toughness and strength.

10 [0035] In the production method of the precipitation hardened Co-Ni based heat-resistant alloy of the present invention, the heat-resistant alloy is subjected to an aging heat treatment by heating for 0.5 to 16 hours to a temperature of 600 to 800°C in a condition of applying stress in order to form a fine twin structure having an average grain size of several microns and to precipitate Co_3Mo or Co_7Mo_6 of sizes from several microns to several tens of nanometers in boundaries between the fine twin structure and a parent phase. The applied stress in the aging heat treatment is preferably about 100 to 400MPa. An applied stress less than 100MPa fails to sufficiently precipitate fine Co_3Mo or Co_7Mo_6 in boundaries between a fine twin structure and a parent phase. The applied stress exceeding 400MPa results in saturation and transforms the alloy which is subjected to the aging heat treatment.

15 [0036] In the production method of the precipitation hardened Co-Ni based heat-resistant alloy of the present invention, the heat-resistant alloy is subjected to an aging heat treatment by heating for 0.5 to 16 hours at a temperature of 600 to 800°C because a temperature lower than 600°C or a time shorter than 0.5 hours fails to sufficiently precipitate a fine twin structure and fine Co_3Mo or Co_7Mo_6 in boundaries between the fine twin structure and a parent phase, and a temperature higher than 800°C or a time longer than 16 hours results in saturation and makes the precipitates rather coarse, thereby causing decrease in strength, and this also causes greater creep elongation by causing decrease in hardness and strength by causing the dislocation to reform when the aging heat treatment is additionally performed after performing a cold working or a warm working having a reduction ratio of not less than 40%.

20 [0037] In the production method of the precipitation hardened Co-Ni based heat-resistant alloy of the present invention, the heat-resistant alloy is subjected to a cold working or a warm working having a reduction ratio of not less than 40% before an aging heat treatment in a condition of applying stress because forming dislocations at high density is necessary, and a density lower than 40% fails to form dislocations at high density. By an aging heat treatment after forming the dislocations at high density, solute atoms such as Mo and Fe are segregated in stacking faults formed between half-dislocations of extended dislocations; thus, the dislocation movements are blocked so that stress relaxation, that is, reoccurrence of dislocations, is suppressed. As a result, a heat-resistant alloy which has high strength and which can inhibit decrease in strength even after a long-period of use under high temperatures can be obtained, combined with an effect in which a fine twin structure forms and fine Co_3Mo or Co_7Mo_6 precipitates in boundaries between the fine twin structure and a parent phase.

25 [0038] In a production method of the precipitation hardened Co-Ni based heat-resistant alloy of the present invention, the heat-resistant alloy is subjected to an aging heat treatment by heating for 0.5 to 16 hours at a higher temperature of 800°C to 950°C after the cold working or warm working having a reduction ratio of not less than 40% after the solid solution heat treatment because a fine twin structure having average grain size of several microns must be formed and Co_3Mo or Co_7Mo_6 of sizes from several microns to several tens of nanometers must be precipitated in boundaries between the fine twin structure and a parent phase. Although aging heat treatments are performed in a condition of applying stress in another production method of the precipitation hardened Co-Ni based heat-resistant alloy of the present invention, an aging heat treatment is performed at a higher temperature of 800°C to 950°C instead of using the condition of applying stress in this production method of the precipitation hardened Co-Ni based heat-resistant alloy of the present invention. In this production method, the aging heat treatment is performed at a higher temperature of 800°C or more and for not less than 0.5 hours because a temperature below 800°C or a time shorter than 0.5 hours fails to sufficiently precipitate a fine twin structure and fine Co_3Mo or Co_7Mo_6 in boundaries between the fine twin structure and a parent phase. Furthermore, the aging heat treatment is performed at a temperature not more than 950°C and for not more than 16 hours because a temperature higher than 950°C or a time longer than 16 hours results in saturation and makes the precipitates solve or become coarse, thereby causing decrease in strength.

30 [0039] In one example of the production method of the precipitation hardened Co-Ni based heat resistant alloy of the present invention, the alloy is melted and prepared through a typical method by using a vacuum high-frequency induction furnace, etc., and is forged into an ingot through a typical forging method. In one example, thereafter, the ingot is subjected to a hot working and solid solution heat treatment at 1000 to 1200°C, and the ingot is then subjected to an aging heat treatment by heating for 0.5 to 16 hours at a temperature of 600 to 800°C in a condition of applying stress of 100 to 140MPa. In another example, thereafter, the alloy is subjected to a cold working or warm working

having a reduction ratio of not less than 40% after the above-mentioned solid solution heat treatment, and then the alloy is subjected to an aging heat treatment by heating for 0.5 to 16 hours at a temperature of 600 to 800°C in a condition of applying stress of 100 to 140MPa. In another example, thereafter, the alloy is subjected to a cold working or warm working having a reduction ratio of not less than 40% after the above-mentioned solid solution heat treatment, and then the alloy is subjected to an aging heat treatment by heating for 0.5 to 16 hours at a temperature of 800°C to 950°C.

[0040] The precipitation hardened Co-Ni based heat-resistant alloys of the present invention may be applied to parts and devices such as exhaust-related parts such as engine exhaust manifolds, peripheral devices of gas turbines, furnace chamber materials, heat-resistant springs and heat-resistant bolts, for which Inconel X750 or Inconel X718 has been used. They may also be used for parts and devices used under higher temperatures. Specifically, they may be preferably applied to springs and bolts in which stress is usually applied in high temperatures.

EXAMPLES

[0041] The following description will discuss the present invention based upon examples.

Example 1

[0042] Alloys of examples of the present invention and comparative examples, which have the compositions shown in the following Table 1, were melted and prepared through a typical method by using a vacuum high-frequency induction furnace to obtain ingots of 50 kg. These ingots were formed into cylindrical bars each having a diameter of 20 mm through a hot forging process. Those bars were subjected to a solution heat treatment at 1100°C, and then to an aging heat treatment of 720°C × 8 hours at a tensile stress of 200MPa. Tensile test pieces having a diameter of 8 mm at parallel portions were obtained from these elements, and these were subjected to tensile tests at room temperature to measure tensile strength. In addition, creep test pieces having a diameter of 6 mm at parallel portions with a distance between scores of 30 mm were obtained, and these were subjected to creep tests in which a stress of 330 MPa was applied thereto at 700°C to measure the elongation 1000 hours later. Table 2 shows the results of these tests. Table 2 shows the observation result of precipitates as a microstructure.

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Table 1

		(mass%)															
No.		C	Si	Mn	Ni	Cr	Mo	W	Mo+1/2W	Nb	Fe	Ti	REM	B	Mg	Zr	Co
Examples of the Present Invention	1	0.03	0.1	0.3	38.3	19.2	12.3	1.2	12.9	0.8	2.4	—	—	0.003	—	—	Balance
	2	0.01	0.2	0.4	42.5	21.0	17.8	—	17.8	1.1	0.9	0.6	—	—	0.002	—	Balance
	3	0.03	0.2	0.7	32.4	16.8	13.7	0.6	14.0	0.3	0.6	2.3	—	0.003	—	0.02	Balance
	4	0.02	0.1	0.2	27.8	18.3	11.5	—	11.5	1.4	1.6	0.5	—	0.002	0.001	—	Balance
	5	0.01	0.3	0.3	30.9	20.1	8.9	2.8	10.3	2.4	4.6	—	0.02	0.005	—	—	Balance
	6	0.02	0.4	0.2	38.6	19.1	14.9	—	14.9	1.0	1.7	0.8	—	0.003	—	0.03	Balance
	7	0.02	0.2	0.1	35.0	13.9	15.4	—	15.4	2.3	2.1	—	0.02	—	0.003	0.04	Balance
Comparative Examples	1	0.01	0.3	0.2	39.4	15.6	8.1	—	8.1	1.9	2.1	—	—	0.002	—	—	Balance
	2	0.02	0.2	0.3	40.9	22.4	7.6	0.8	8.0	0.5	1.6	1.0	—	0.001	—	—	Balance
	3	0.01	0.4	0.6	29.7	19.1	9.0	—	9.0	2.2	3.8	0.4	—	—	0.003	—	Balance
	4	0.01	0.1	0.5	33.3	18.5	7.9	0.5	8.15	—	—	2.1	0.01	0.003	—	0.02	Balance

Table 2

	No.	Precipitations by aging treatment	Tensile strength at room temperature (MPa)	Creep elongation 1000 hours later (%) Conditions: 700°C 330MPa
Examples of the Present Invention	1	CO ₇ Mo ₆	1217	2.3
	2	CO ₇ Mo ₆	1303	2.0
	3	CO ₇ Mo ₆	1240	2.2
	4	CO ₇ Mo	1121	2.7
	5	CO ₇ Mo	1144	2.7
	6	CO ₇ Mo ₆	1252	2.2
	7	CO ₇ Mo ₆	1299	2.1
Comparative Examples	1	—	895	rupture
	2	—	881	rupture
	3	—	976	rupture
	4	—	924	rupture

Example 2

[0043] Cylindrical bars having a diameter of 20 mm of No. 5 and No. 6 alloy of the present invention shown in Table 1 were subjected to a solid solution heat treatment at 1100°C. Then, as examples of the present invention, the cylindrical bars were subjected to an aging heating treatment of 620°C × 15 hours at a tensile stress of 250MPa, an aging heat treatment of 720°C × 8 hours at a tensile stress of 200MPa, or an aging heat treatment of 770°C × 4 hours at a tensile stress of 120MPa. As comparative examples, the cylindrical bars were subjected to an aging heating treatment of 850°C × 4 hours at a tensile stress of 80MPa, or an aging heat treatment of 550°C × 15 hours at a tensile stress of 250MPa. Creep test pieces were obtained from these elements in the same manner as in Example 1, and creep tests were carried out under the same conditions as in Example 1 to measure creep. Table 3 shows the results of the tests.

Table 3

	No.	Used alloys	Applied stress in aging heat treatment (MPa)	Aging heat treatment conditions	Creep elongation 1000 hours later (%) Conditions: 700°C 330MPa
Examples of the Present Invention	8	Example 5 of the present invention	250	620°C × 15hr	2.6
	9	Example 5 of the present invention	200	720°C × 8hr	2.7
	10	Example 5 of the present invention	120	770°C × 4hr	2.9
	11	Example 6 of the present invention	250	620°C × 15hr	2.0
	12	Example 6 of the present invention	200	720°C × 8hr	2.2
	13	Example 6 of the present invention	120	770°C × 4hr	2.4
Comparative Examples	5	Example 5 of the present invention	80	850°C × 4hr	rupture
	6	Example 6 of the present invention	250	550°C × 15hr	4.6

Example 3

5 [0044] Cylindrical bars having a diameter of 20 mm of No. 5 and No. 6 alloy of the present invention shown in Table 1 were subjected to a solid solution heat treatment at 1100°C. Then, as examples of the present invention, the cylindrical bars were subjected to a cold working at reduction ratios of 45, 60 or 75%, and were then subjected to an aging heat treatment under conditions shown in Table 4 (applied stress, heating temperature and heating time). As a comparative example, the cylindrical bars were subjected to a cold working at a reduction ratio of 45%, and were then subjected to an aging heat treatment of 720°C ×8 hours in an unloaded condition. Moreover, as another comparative example, the cylindrical bars were subjected to a cold working at a reduction ratio of 60%, and were then subjected to an aging heat treatment of 720°C ×8 hours in an unloaded condition. Creep test pieces were obtained from these elements in the same manner as in Example 1, and creep tests were carried out under the same conditions as in Example 1 to measure creep. Table 4 shows the results of the tests.

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Table 4

	No.	Alloys used	Cold working ratio (%)	Applied stress in aging heat treatment (MPa)	Aging heat treatment conditions	Creep elongation 1000 hours later (%)
Examples of the Present Invention	14	Example 5 of the present invention	45	400	720°C × 8hr	1.8
	15	Example 5 of the present invention	45	350	770°C × 4hr	1.9
	16	Example 5 of the present invention	60	400	700°C × 8hr	1.3
	17	Example 5 of the present invention	60	350	720°C × 4hr	1.5
	18	Example 5 of the present invention	75	400	650°C × 8hr	1.0
	19	Example 5 of the present invention	75	350	650°C × 4hr	1.2
	20	Example 6 of the present invention	45	400	650°C × 8hr	1.0
	21	Example 6 of the present invention	60	400	650°C × 8hr	0.9
	22	Example 6 of the present invention	75	400	650°C × 8hr	1.2

Table 4 (continued)

	No.	Alloys used	Cold working ratio (%)	Applied stress in aging heat treatment (MPa)	Aging heat treatment conditions	Creep elongation 1000 hours later (%)
Comparative Examples	7	Example 5 of the present invention	45	—	700°C × 4hr	4.8
	8	Example 5 of the present invention	60	—	720°C × 8hr	4.6
Creep elongation was measured by creep tests carried out under conditions of 700°C, 330MPa						

Example 4

[0045] Cylindrical bars having a diameter of 20 mm of No. 5 and No. 6 alloy of the present invention shown in Table 1 were subjected to a solid solution heat treatment at 1100°C. Then, as examples of the present invention, the cylindrical bars were subjected to a cold working at reduction ratios of 60 or 75%, and were then subjected to an aging heat treatment of 850°C ×4 hours or 920°C ×2 hours in an unloaded condition. As a comparative example, the cylindrical bars were subjected to a cold working at a reduction ratio of 35%, and were then subjected to an aging heat treatment of 920°C ×2 hours in an unloaded condition. Moreover, as another comparative example, the cylindrical bars were subjected to a cold working at a reduction ratio of 75%, and were then subjected to an aging heat treatment of 990°C ×2 hours in an unloaded condition. Creep test pieces were obtained from these elements in the same manner as in Example 1, and creep tests were carried out under the same conditions as in Example 1 to measure creep. Table 5 shows the results of the tests.

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Table 5

	No.	Alloys used	Cold working ratio (%)	Applied stress in aging heat treatment (MPa)	Aging heat treatment conditions	Creep elongation 1000 hours later (%)
Examples of the Present Invention	23	Example 5 of the present invention	60	—	850°C × 4hr	1.7
	24	Example 5 of the present invention	60	—	920°C × 2hr	1.9
	25	Example 5 of the present invention	75	—	850°C × 4hr	1.4
	26	Example 5 of the present invention	75	—	920°C × 2hr	1.5
	27	Example 6 of the present invention	60	—	920°C × 4hr	1.7
	28	Example 6 of the present invention	75	—	850°C × 2hr	1.3
Comparative Examples	9	Example 5 of the present invention	35	—	920°C × 2hr	4.6
	10	Example 5 of the present invention	75	—	990°C × 2hr	rupture
Creep elongation was measured by creep tests carried out under conditions of 700°C, 330MPa						

[0046] According to the above-mentioned results, in the Examples No. 1 to 7 of the present invention (Table 2), fine twin structure was formed when the structures of test pieces were observed by a SEM (scanning electron microscope). Moreover, Co_7Mo_6 or Co_3Mo was precipitated in boundaries between the fine twin structure and a parent phase. Furthermore, the tensile strength at room temperature was set in a range of 1121 to 1303 MPa, and the creep elongation was 2.0 to 2.7%.

[0047] In contrast, in the case of Comparative Examples 1 to 3 in which the Mo+1/2W content was less than that of the present invention, and in the case of Comparative Example 4 in which the Mo+1/2W content was less than that of the present invention and Nb and Fe was not contained, Co_7Mo_6 or Co_3Mo was not precipitated, the tensile strength at room temperature was set in a range of 881 to 976 MPa, that is, 87% of that of the present invention, and all test pieces were ruptured in the creep test.

[0048] In the Example No. 8 to 13 of the present invention (Table 3), fine twin structure was formed when the structures of test pieces were observed by a SEM (scanning electron microscope). Moreover, Co_3Mo or Co_7Mo_6 was precipitated in boundaries between the fine twin structure and a parent phase. Furthermore, the creep elongation in the creep test was 2.0 to 2.9%.

[0049] In contrast, in the case of Comparative Example 5 in which the temperature of the aging heat treatment was higher than that of the present invention, and in the case of Comparative Example 6 in which the temperature of the aging heat treatment was lower than that of the present invention, Co_3Mo or Co_7Mo_6 was not precipitated, test pieces were ruptured in the creep test in the Comparative Example 5, and the creep elongation in the creep test was 4.6% in the Comparative Example 6, that is, improvement of creep strength was not observed.

[0050] In the Examples No. 14 to 22 of the present invention (Table 4), fine twin structure was formed when the structures of test pieces were observed by a SEM (scanning electron microscope). Moreover, Co_3Mo or Co_7Mo_6 was precipitated in boundaries between the fine twin structure and a parent phase. Fig. 1 and Fig. 2 show structure photographs of the Example No. 22 of the present invention. By these structural micrographs, structure of Example No. 22 of the present invention was a structure in which massive Co_3Mo or Co_7Mo_6 was precipitated in boundaries between a fine twin structure of equilateral triangle and a parent phase. Furthermore, the creep elongations in the creep test in the Examples No. 14 to 22 of the present invention were 0.9 to 1.9%. These creep elongations were smaller than that of the Comparative Examples No. 7 to 13 in which cold working or a warm working having a reduction ratio of not less than 40 % was not performed before the aging heat treatment.

[0051] In contrast, in the case of Comparative Examples 7 and 8 in which the aging heat treatment was performed in an unloaded condition, Co_3Mo or Co_7Mo_6 was not precipitated, and the creep elongations in the creep tests were respectively 4.8% and 4.6%, that is, improvements creep strength were not observed.

[0052] In the Examples No. 23 to 28 of the present invention (Table 5), fine twin structure was formed when the structure of test pieces was observed by a SEM (scanning electron microscope). Moreover, Co_3Mo or Co_7Mo_6 was precipitated in boundaries between the fine twin structure and a parent phase. Furthermore, the creep elongations in the creep tests in the Examples No. 23 to 28 of the present invention were 1.3 to 1.9%, that is, almost equivalent to those of the Examples No. 14 to 22 of the present invention (Table 4; Example 3).

[0053] In contrast, in the case of Comparative Example 9 in which the cold reduction ratio was lower than that of the present invention, Co_3Mo or Co_7Mo_6 was not precipitated, and the creep elongation in the creep test was 4.6%, that is, improvement of creep strength was not observed. Moreover, in the case of Comparative Example 10 in which the temperature of the aging heat treatment was higher than that of the present invention, test pieces ruptured in the creep test. Recrystallization structure was formed when the structure of test pieces was observed, confirming disappearance of the fine twin structure and the precipitates.

Claims

1. A precipitation hardened Co-Ni based heat-resistant alloy comprising by weight:

not more than 0.05% of C; not more than 0.5% of Si; not more than 1.0% of Mn; 25 to 45% of Ni; 13 to 22% of Cr; 10 to 18% of Mo or 10 to 18% of Mo + 1/2W; 0.1 to 5.0% of Nb; 0.1 to 5.0% of Fe; at least one kind of 0.007 to 0.10% of REM; 0.001 to 0.010% of B; 0.0007 to 0.010% of Mg and 0.001 to 0.20% of Zr;

the balance of Co and inevitable impurities;

a fine twin structure;

a parent phase; and

Co_3Mo or Co_7Mo_6 precipitated at boundaries of the fine twin structure and the parent phase.

2. A precipitation hardened Co-Ni based heat-resistant alloy comprising by weight:

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not more than 0.05% of C; not more than 0.5% of Si; not more than 1.0% of Mn; 25 to 45% of Ni; 13 to 22% of Cr; 10 to 18% of Mo or 10 to 18% of Mo + 1/2W; 0.1 to 5.0% of Nb; 0.1 to 5.0% of Fe; 0.1 to 3.0% of Ti; at least one kind of 0.007 to 0.10% of REM; 0.001 to 0.010% of B; 0.0007 to 0.010% of Mg and 0.001 to 0.20% of Zr;

the balance of Co and inevitable impurities;

a fine twin structure;

a parent phase; and

Co₃Mo or Co₇Mo₆ precipitated at boundaries of the fine twin structure and the parent phase.

3. A production method for precipitation hardened Co-Ni based heat-resistant alloy, the method comprising the steps of:

preparing an alloy comprising by weight:

not more than 0.05% of C; not more than 0.5% of Si; not more than 1.0% of Mn; 25 to 45% of Ni; 13 to 22% of Cr; 10 to 18% of Mo or 10 to 18% of Mo + 1/2W; 0.1 to 5.0% of Nb; 0.1 to 5.0% of Fe; at least one kind of 0.007 to 0.10% of REM; 0.001 to 0.010% of B; 0.0007 to 0.010% of Mg and 0.001 to 0.20% of Zr; and

the balance of Co and inevitable impurities;

subjecting the alloy to a solid solution heat treatment; and

subjecting the alloy to an aging heat treatment at 600 to 800°C for 0.5 to 16 hours in a condition of applying stress, thereby forming a fine twin structure in a parent phase, and precipitating Co₃Mo or Co₇Mo₆ at a boundary of the fine twin structure and the parent phase.

4. A production method for precipitation hardened Co-Ni based heat-resistant alloy, the method comprising the steps of:

preparing an alloy comprising by weight:

not more than 0.05% of C; not more than 0.5% of Si; not more than 1.0% of Mn; 25 to 45% of Ni; 13 to 22% of Cr; 10 to 18% of Mo or 10 to 18% of Mo + 1/2W; 0.1 to 5.0% of Nb; 0.1 to 5.0% of Fe; 0.1 to 3.0% of Ti; at least one kind of 0.007 to 0.10% of REM; 0.001 to 0.010% of B; 0.0007 to 0.010% of Mg and 0.001 to 0.20% of Zr; and

the balance of Co and inevitable impurities;

subjecting the alloy to a solid solution heat treatment; and

subjecting the alloy to an aging heat treatment at 600 to 800°C for 0.5 to 16 hours in a condition of applying stress, thereby forming a fine twin structure in a parent phase, and precipitating Co₃Mo or Co₇Mo₆ at a boundary of the fine twin structure and the parent phase.

5. A production method for precipitation hardened Co-Ni based heat-resistant alloy, the method comprising the steps of:

preparing an alloy comprising by weight:

not more than 0.05% of C; not more than 0.5% of Si; not more than 1.0% of Mn; 25 to 45% of Ni; 13 to 22% of Cr; 10 to 18% of Mo or 10 to 18% of Mo + 1/2W; 0.1 to 5.0% of Nb; 0.1 to 5.0% of Fe; at least one kind of 0.007 to 0.10% of REM; 0.001 to 0.010% of B; 0.0007 to 0.010% of Mg and 0.001 to 0.20% of Zr; and

the balance of Co and inevitable impurities;

subjecting the alloy to a solid solution heat treatment;

subjecting the alloy to a cold working or a warm working having a reduction ratio of not less than 40%; and

subjecting the alloy to an aging heat treatment at 600 to 800°C for 0.5 to 16 hours in a condition of applying stress, thereby forming a fine twin structure in a parent phase, and precipitating Co₃Mo or Co₇Mo₆ at a boundary of the fine twin structure and the parent phase.

6. A production method for precipitation hardened Co-Ni based heat-resistant alloy, the method comprising the steps of:

preparing an alloy comprising by weight:

5 not more than 0.05% of C; not more than 0.5% of Si; not more than 1.0% of Mn; 25 to 45% of Ni; 13 to 22% of Cr; 10 to 18% of Mo or 10 to 18% of Mo + 1/2W; 0.1 to 5.0% of Nb; 0.1 to 5.0% of Fe; 0.1 to 3.0% of Ti; at least one kind of 0.007 to 0.10% of REM; 0.001 to 0.010% of B; 0.0007 to 0.010% of Mg and 0.001 to 0.20% of Zr; and

the balance of Co and inevitable impurities;

subjecting the alloy to a solid solution heat treatment;

10 subjecting the alloy to a cold working or a warm working having a reduction ratio of not less than 40%; and

subjecting the alloy to an aging heat treatment at 600 to 800°C for 0.5 to 16 hours in a condition of applying stress, thereby forming a fine twin structure in a parent phase, and precipitating Co_3Mo or Co_7Mo_6 at a boundary of the fine twin structure and the parent phase.

- 15 **7.** A production method for precipitation hardened Co-Ni based heat-resistant alloy, the method comprising the steps of:

preparing an alloy comprising by weight:

20 not more than 0.05% of C; not more than 0.5% of Si; not more than 1.0% of Mn; 25 to 45% of Ni; 13 to 22% of Cr; 10 to 18% of Mo or 10 to 18% of Mo + 1/2W; 0.1 to 5.0% of Nb; 0.1 to 5.0% of Fe; at least one kind of 0.007 to 0.10% of REM; 0.001 to 0.010% of B; 0.0007 to 0.010% of Mg and 0.001 to 0.20% of Zr; and

the balance of Co and inevitable impurities;

subjecting the alloy to a solid solution heat treatment;

25 subjecting the alloy to a cold working or a warm working having a reduction ratio of not less than 40%; and

subjecting the alloy to an aging heat treatment at 800°C to 950°C for 0.5 to 16 hours, thereby forming a fine twin structure in a parent phase, and precipitating Co_3Mo or Co_7Mo_6 at a boundary of the fine twin structure and the parent phase.

- 30 **8.** A production method for precipitation hardened Co-Ni based heat-resistant alloy, the method comprising the steps of:

preparing an alloy comprising: all by weight,

35 not more than 0.05% of C; not more than 0.5% of Si; not more than 1.0% of Mn; 25 to 45% of Ni; 13 to 22% of Cr; 10 to 18% of Mo or 10 to 18% of Mo + 1/2W; 0.1 to 5.0% of Nb; 0.1 to 5.0% of Fe; 0.1 to 3.0% of Ti; at least one kind of 0.007 to 0.10% of REM; 0.001 to 0.010% of B; 0.0007 to 0.010% of Mg and 0.001 to 0.20% of Zr; and

the balance of Co and inevitable impurities;

subjecting the alloy to a solid solution heat treatment;

40 subjecting the alloy to a cold working or a warm working having a reduction ratio of not less than 40%; and

subjecting the alloy to an aging heat treatment at 800°C to 950°C for 0.5 to 16 hours, thereby forming a fine twin structure in a parent phase, and precipitating Co_3Mo or Co_7Mo_6 at a boundary of the fine twin structure and the parent phase.

Fig. 1



× 5000

Fig. 2



× 20000



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 03 01 5101

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	WO 02 24967 A (NHK SPRING CO. LTD.) 28 March 2002 (2002-03-28) *whole document* -----	1-8	C22C19/05 C22F1/10
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C22C C22F
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 3 October 2003	Examiner Badcock, G
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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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 01 5101

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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03-10-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0224967 A	28-03-2002	JP 2002097537 A	02-04-2002
		EP 1329528 A1	23-07-2003
		WO 0224967 A1	28-03-2002

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