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(71) Applicant: NHK Spring Co., Ltd. Yokohama-shi, Kanagawa 236-0004 (JP)

(72) Inventors:

Chiba, Akihiko
 Morioka-shi, Iwate 020-0066 (JP)

 Takeda, Shirou Kitakami-shi, Iwate 024-0333 (JP) Sato, Shigemi c/o NHK SPRING CO., LTD. Yokohama-shi, Kanagawa 236-0004 (JP)

 Ueta, Shigeki Chita-shi, Aichi 478-0035 (JP)

 Noda, Toshiharu Tajimi-shi, Gifu 507-0826 (JP)

 Okabe, Michio Chita-shi, Aichi 478-0044 (JP)

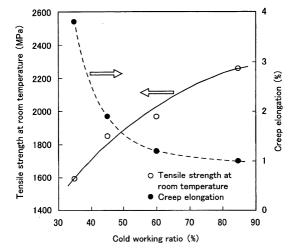
(74) Representative: Nöth, Heinz Patent Attorney, Arnulfstrasse 25 80335 München (DE)

(54) CO-NI BASE HEAT-RESISTANT ALLOY AND METHOD FOR PRODUCTION THEREOF

(57) A Co-Ni base heat-resistant alloy is composed of, 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 one kind or more 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, with the balance of substantially Co and inevitable impurities.

Fig. 1



Description

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FIELD OF THE INVENTION

[0001] The present invention relates to a Co-Ni base heat-resistant alloy and to a preparation method therefor, and more particularly concerns a Co-Ni base heat-resistant alloy that is used for springs, bolts, etc., that are employed to portions, such as engines and exhaust systems and peripheral devices of gas turbines, which are exposed to high temperatures, and to a preparation method therefor.

BACKGROUND OF THE INVENTION

[0002] Conventionally, heat-resistant parts that are employed in portions, such as engines and exhaust systems and peripheral devices of gas turbines, that are exposed to high temperatures, are manufactured by using Ni-base super heat-resistant alloy 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%).

[0003] These Ni-base super-heat-resistant alloys are reinforced by depositing γ ' (Ni₃ (Al, Ti, Nb) and γ " (Ni₃Nb). However, in the case of long-period of use at high temperatures of not less than 600°C, γ ' and γ " become coarse due to overaging, causing degradation in the strength. Moreover, parts such as springs and bolts on which stress is continuously imposed are subjected to great stress relaxation, failing to maintain performances originally required for the parts.

[0004] Therefore, objects of the present invention are to provide a heat resistant alloy which exhibits higher strength than the above-mentioned Ni-base super-heat-resistant alloy, and is less susceptible to degradation in the strength even after a long-period of use under high temperatures, and to provide a preparation method therefor.

DISCLOSURE OF THE INVENTION

[0005] In order to solve the above-mentioned problems, the inventors of the present invention have carried out various research and studies to find a heat-resistant alloy that has higher strength and is less susceptible to degradation in strength even after long-period of use under high temperatures in comparison with the Ni-base super-heat-resistant alloys, and have found that a Co-Ni-Cr based alloy is usable as the heat-resistant alloy, and that since this Co-Ni-Cr based alloy has a very low stacking fault energy so that when this is subjected to cold working or warm working, a solute element such as Mo, Fe and Nb is segregated in stacking faults of extended dislocation to block dislocation movements and consequently to achieve a high work hardening performance, and that when this is aged subsequently after the cold working or the warm working with working strain remaining therein, the strength is further improved.

[0006] Moreover, with respect to the alloy having the above-mentioned reinforced mechanism, for example, Japanese Unexamined Patent Application Publication No. 10-140279 has disclosed such an alloy; however, since this is still not sufficient in strength under high temperatures, a σ phase is deposited when this alloy is strengthened by increasing the amount of solute elements such as Mo, Fe, and Nb therein, resulting in degradation in workability and toughness. The inventors of the present invention have found that in order to solve this problem, when Cr is set to be a minimum level that is required for use in a heat-resistant environment of not more than 750°C, it is possible to suppress the deposition of the σ phase even when the amount of solute elements such as Mo, Fe, and Nb is increased, and that it is possible to further increase the strength by adding W thereto.

⁴⁵ **[0007]** The present invention has been devised based upon these findings. Here, in the following explanation "%" refers to mass%.

[0008] In other words, the Co-Ni base heat-resistant alloy of the present invention contains C: not more than 0.05%, Si: not more than 0.5%, Mn: not more than 1.0%, Ni: 25 to 45%, Cr: 13 to less than 18%, Mo + 1/2W of one kind or two kinds of Mo and W: 7 to 20%, Ti: 0.1 to 3.0%, Nb: 0.1 to 5.0% and Fe: 0.1 to 5.0%, with the rest being composed of Co and inevitable impurities.

[0009] Furthermore, the present invention preferably contains at least one selected from the group consisting of REM (at least one rare-earth elements such as Y, Ce, and misch metal): 0.007 to 0.10%, B: 0.001 to 0.010%, Mg: 0.0007 to 0.010% and Zr: 0.001 to 0.20%.

[0010] Moreover, the preparation method of the Co-Ni base heat-resistant alloy of the present invention is characterized by the steps in which: an alloy containing C: not more than 0.05%, Si: not more than 0.5%, Mn: not more than 1.0%, Ni: 25 to 45%, Cr: 13 to less than 18%, Mo + 1/2W of one kind or two kinds of Mo and W: 7 to 20%, Ti: 0.1 to 3.0%, Nb: 0.1 to 5.0% and Fe: 0.1 to 5.0%, and the rest being composed of Co and inevitable impurities, is subjected to a solid solution heat treatment at 1000 to 1200°C or a hot working at this temperature, and this is then subjected to

a cold working or a warm working having a working ratio of not less than 40%, and this is then subjected to an aging heat treatment at 500 to 800°C for 0.1 to 50 hours.

[0011] Moreover, in the above-mentioned preparation method also, the alloy is preferably allowed to contain at least one selected from the group consisting of REM (at least one rare-earth elements such as Y, Ce, and misch metal): 0.007 to 0.10%, B: 0.001 to 0.010%, Mg: 0.0007 to 0.010% and Zr: 0.001 to 0.20%.

[0012] Next, the following description will discuss the reasons for the above-mentioned limitations to the component composition in the Co-Ni base heat-resistant alloy and the preparation method of the present invention. C: Not more than 0.05%

[0013] Carbon C is bound to Nb and Ti to form carbides to prevent crystal particles 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 set to be not less than 0.005%; however, since a content exceeding 0.05%, more specifically, 0.03%, would cause degradation in the toughness and corrosion resistance, and would also form a carbide with a dislocation anchoring element such as Mo, resulting in interference with the dislocation anchoring, the content is set to be not more than 0.05%. The preferable range is set to be 0.005 to 0.03%. Si: Not more than 0.5%

[0014] 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 degradation in the toughness, the content is set to be not more than 0.5%. The preferable range is set to be not more than 0.3%. Mn: 0.1 to 1.0%

[0015] 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. In order to obtain these effects, the content must be set to be not less than 0.1%, more preferably, 0.25%; however, since a content exceeding 1.0%, more specifically, 0.7%, would cause degradation in the corrosion resistance, the content is set to be 0.1 to 1.0%. The preferable range is set to be 0.25 to 0.7%.

Ni: 25 to 45%

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[0016] 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 be set to be not less than 25%, more preferably, 27%; however, since a content exceeding 45%, more specifically, 33%, would cause degradation in the work hardening performance, the content is set to be 25 to 45%. The preferable range is set to be 27 to 33%.

Cr: 13% to less than 18%

[0017] 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 be set to be not less than 13%, more preferably, 14.5%; however, since a content exceeding 18%, more specifically, 17%, tends to cause deposition of a σ phase, the content is set to be in a range of 13 to less than 18%. The preferable range is set to be 14.5 to 17%.

Mo + 1/2W: 7 to 20%

[0018] 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 be set to be not less than 7%, more preferably, 9%; however, since the total amount of the content of Mo and 1/2 of the content of W exceeds 20%, more specifically, 16%, tends to cause deposition of a σ phase, the content is set in a range of 7 to 20%. The preferable range is set to be 9 to 16%.

Ti: 0.1 to 3.0%

[0019] Since Ti improves the strength, this element is contained for this purpose. In order to obtain this effect, the content must be set to be not less than 0.1%, more preferably, 0.5%; however, since a content exceeding 3.0%, more specifically, 1.8%, would cause deposition of an η phase (Ni $_3$ Ti) resulting in degradation in the workability and toughness, the content is set to be in a range of 0.1 to 3.0%. The preferable range is set to be 0.5 to 1.8%.

Nb:0.1 to 5.0%

[0020] Nb is bound to C to form carbides to prevent crystal particles from becoming coarse at the time of 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 be set to be not less than 0.1%, more preferably, 0.5%; however, since the content exceeding 5.0%, more specifically, 3.5%, would cause deposition of a σ phase (Ni₃Nb) resulting in degradation in the workability and toughness, the content is set to be in a range of 0.1 to 5.0%. The preferable range is set to be 0.5 to 3.5%.

Fe: 0.1 to 5.0%

[0021] 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 be set to be not less than 0.1%, more preferably, 0.5%; however, since a content exceeding 5.0%, more specifically, 3.3%, causes degradation in the oxidation resistance property, the content is set to be in a range of 0.1 to 5.0%. The preferable range is set to be 0.5 to 3.3%.

[0022] Here, 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. REM: 0.007 to 0.10%

[0023] 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 be set to be not less than 0.007%, more preferably, 0.01%; however, since the content exceeding 0.10%, more specifically, 0.04%, causes degradation in the hot workability and oxidation resistance property in an inverse manner, the content is set to be in a range of 0.007 to 0.10%. The preferable range is set to be 0.01 to 0.04%. B: 0.001 to 0.010%, Mg: 0.0007 to 0.010%, Zr: 0.001 to 0.20%.

[0024] 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 set to be 0.001%, more preferably, 0.002%, Mg must be set to be 0.0007%, more preferably, 0.001%, and Zr must be set to be 0.001%, more preferably, 0.01%; however, since B exceeding 0.010%, more specifically, 0.004%, Mg exceeding 0.010%, more specifically, 0.003% and Zr exceeding 0.20%, more specifically 0.03%, would cause degradation in the hot workability and oxidation resistance property, the ranges of the contents are respectively set to be in the above-mentioned ranges. More preferably, B is set to be in a range of 0.002 to 0.004%, Mg is set to be in a range of 0.001 to 0.003%, and Zr is set to be in a range of 0.01 to 0.03%.

Co: Balance

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[0025] 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.

[0026] Next, the following description will discuss the preparation method of the Co-Ni base heat-resistant alloy of the present invention and the reasons for the above-mentioned limitations to heat treatment and working conditions.

[0027] In the preparation method of the Co-Ni base heat-resistant alloy of the present invention, solute atoms such as Mo are segregated at stacking faults between extended dislocations which have been introduced through cold or warm working so as to interfere with dislocation movements so that by suppressing the reoccurrence of dislocations, the Co-Ni base heat-resistant alloy having the above-mentioned component composition is strengthened. Therefore, in the preparation method of the Co-Ni base heat-resistant alloy material of the present invention, the above-mentioned Co-Ni base heat-resistant alloy is subjected to a solid solution heat treatment at 1000 to 1200°C to make the organization homogenous, or a hot working at a temperature of not less than 1000°C to make the crystal grains finer, and this is then subject to cold working or warm working at a temperature of a working ratio of not less than 40% so that a great number of the dislocations are introduced to carry out work hardening. Here, the warm working may be carried out during a cooling process after the solid solution heat treatment or the hot working. Thereafter, an aging heat treatment is carried out for 0.1 to 50 hours at 500 to 800°C so that 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.

[0028] The reason that in the preparation method of the above-mentioned Co-Ni base heat-resistant alloy, the solid solution heat treatment or the hot working is carried out at 1000 to 1200°C is because a temperature lower than 1000°C fails to provide a sufficiently homogenous structure and also fails to lower the hardness, causing a difficulty in working. Moreover, this might cause deposition of a compound such as Mo that exerts an anchoring effect on dislocations, and the subsequent reduction in the age hardening property. Moreover, a temperature exceeding 1200°C makes crystal grains coarse, resulting in degradation in the toughness and strength.

[0029] Moreover, the reason that the cold working or warm working having a working ratio of not less than 40% is carried out after the solid solution heat treatment or the hot working is because, as shown in Table 3 and Fig. 1, the working ratio of less than 40% fails to provide a high work hardening perfomance that is exerted by solute elements such as Mo and Fe to be segregated in the stacking faults in extended dislocations to interfere with the dislocation movements, and also causes greater creep elongation.

[0030] Moreover, the reason that the aging heat treatment is carried out at 500 to 800°C for 0.1 to 50 hours after the cold or warm working of a working ratio of not less than 40% is because, as shown in Table 4 and Fig. 2, when the treatment is at less than 500°C or less than 0.1 hour, it fails to increase the strength sufficiently or, when the treatment exceeds 800°C or exceeds 50 hours, the dislocations reform to cause degradation in the hardness and strength, as well as the subsequent greater creep elongation.

[0031] In one example of the preparation method of the Co-Ni base heat resistant alloy of the present invention, the alloy is melted and prepared through a normal method by using a vacuum high-frequency induction furnace, etc., and is forged into an ingot through a normal forging method. Thereafter, this is subjected to a hot working and solid solution heat treatment at 1000 to 1200°C, and this is then subjected to a cold working or warm working having a working ratio of not less than 40%, and is then subjected to an aging heat treatment at 500 to 800°C for 0.1 to 50 hours.

[0032] Moreover, with respect to applications of the Co-Ni base heat-resistant alloy of the present invention, it is 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, in which Inconel X750 or Inconel X718 has been used. It is also applied to parts and devices used under higher temperature.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033]

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FIG. 1 is a graph that shows the relationship between the cold working ratio and the tensile strength at room temperature and creep elongation of the Co-Ni base heat-resistant alloy of the present invention.

FIG. 2 is a graph that shows the relationship between the aging temperature and the tensile strength at room temperature and creep elongation of the Co-Ni base heat-resistant alloy of the present invention.

BEST MODES FOR CARRYING OUT THE INVENTION

[0034] The following description will discuss the present invention based upon examples.

Example 1

[0035] Alloys of an example and a comparative example of the present invention, which have the component compositions shown in the following Table 1, were melted and prepared through a normal method by using a vacuum high-frequency induction furnace to obtain ingots of 30 kg. These ingots were formed into cylindrical bars each having a diameter of 35 mm through a hot forging process. Those bars except for that of comparative example 4 were subjected to a solution heat treatment at 1100° C, and then a cold working at a working ratio of 85% to form cylindrical bars each having a diameter of 13.6 mm, and these were then subjected to an aging of 720° C x 4 hours. Moreover, the bar of comparative example 4 was subjected to a solid solution heat treatment at 1050° C, and was then subjected to an aging treatment of 725° C \times 16 hours at a working ratio of 30%. 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 the tensile strength. Moreover, 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 test 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.

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(mass%)	လ	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	1
) (m	72	1			0.01	0.02	1			1	0.01	ļ	1	1		
	Mg	ı	1	0.001	1	0.002	ı	0.002	1	ı	0.001		1	0.001	1	æ
	8	1	1	0.002	0.002	ı	0.003	0.003	0.002	0.003	0.002	0.002	0.003	0.002	1	AI:0.8
	REM	1		1	ı	ı	0.02	0.01	1	1	ı	1	ı	1	I	
	Fe	2.4	2.1	4.1	0.5	2.1	1.9	3.0	2.3	2.0	1.8	2.2	2.1	2.0	0.3	6.8
	Nb	1.6	1.5	1.7	1.8	4.0	1.9	2.4	0.5	1.2	1.5	1.4	1.6	3.2	0.2	6.0
	Ti	8.0	0.7	0.7	0.8	9.0	1.5	1.8	1.2	1.0	0.7	6.0	0.8	1.0	0.1	2.5
	W		13.6	-	1.8	4.7		2.3	1.9	3.0	_		1	1.8	1	-
	Mo	12.1	1	14.3	14.4	16.5	10.2	9.6	13.7	15.1	14.0	13.8	10.1	14.6	5.2	1
	ర	14.0	15.8	13.3	15.9	16.1	17.8	16.0	13.9	16.2	15.5	16.0	21.0	20.2	19.8	15.0
	Z	29.5	30.3	27.2	32.0	42.3	30.1	30.8	30.4	33.6	29.7	30.9	30.2	31.9	20.6	73.0
	Mn	0.5	0.3	0.6	0.3	0.5	0.4	0.5	9.0	0.4	0.5	0.3	0.3	0.4	0.1	0.7
	:ō	0.2	0.1	0.2	0.3	0.1	0.2	0.1	0.1	0.2	0.2	0.1	0.2	0.2	0.1	0.2
	O	0.02	0.01	0.01	0.01	0.02	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.02	0.01	0.04
	Š.	—	2	က	4	5	9	7	8	6	10	Ξ	-	2	3	4
able 1						Cxamples	The	Present						Comparative	Examples	

Comparative Example 4 relates to Inconel X750.

Table 2

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Creep elongation 1000 hours later (%) Tensile strength at room temperature No. Conditions: 700°C 330 MPa (MPa) 2206 1 1.1 2334 2 0.9 3 2412 0.9 2520 0.8 4 Examples 5 2775 0.7 Of 1.0 The 6 2256 Present 7 2589 8.0 Invention 2560 8 8.0 9 2667 0.8 10 2148 1.1 11 2187 1.1 1 1991 1.6 2 Cracks in cold working Comparative examples 3 1677 1.9

Example 2

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[0036] Cylindrical bars having a diameter of 35 mm of No. 6 alloy of the present invention shown in Table 1 were subjected to a solid solution heat treatment at 1100° C, and were then subjected to cold workings at working ratios of 35%, 45% and 60% (comparative example 5, and examples 12 and 13 of the present invention), and these were then subjected to an aging of 720° C \times 4 hours. Tensile test pieces and creep test pieces were obtained from these elements in the same manner as in example 1, and tensile tests and creep tests were carried out on these under the same conditions as in example 1 to measure the tensile strength and creep. Table 3 and Fig. 1 show the results of the tests.

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Table 3

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	Cold working ratio (%)	Tensile strength at room temperature (MPa)	Creep elongation (%) 1000 hours later			
Comparative example 5	35	1589	3.8			
Example 12 of the present invention	45	1853	1.9			
Example 13 of the present invention	60	1971	1.2			
Example 6 of the present invention	85	2256	1.0			
Creep elongation was measured by creep tests carried out under conditions of 700°C, 330MPa.						

Example 3

[0037] Cylindrical bars having a diameter of 35 mm of No. 10 alloy of the present invention shown in Table 1 were subjected to a solid solution heat treatment at 1100°C and to cold working at working ratio of 85%, and were then subjected to an aging under conditions shown in Table 4 (comparative examples 6 and 7, examples 14 and 15 of the present invention). Tensile test pieces and creep test pieces were obtained from these elements in the same manner

as in example 1, and tensile tests and creep tests were carried out on these under the same conditions as in example 1 to measure the tensile strength and creep. Table 4 and Fig. 2 show the results of the tests.

Table 4

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	Aging temperature (°C)	Heating time (hr)	Tensile strength at room temperature (MPa)	Creep elongation (%) 1000 hours later		
Comparative example 6	450	16	1795	2.1		
Example 14 of the present invention	550	32	2069	1.2		
Example 15 of the present invention	650	16	2226	1.1		
Example 10 of the present invention	720	4	2148	1.1		
Comparative example 7	850	4	1314	4.8		
Creep elongation was measured by creep tests carried out under conditions of 700°C, 330MPa.						

[0038] The results of Table 1 and Table 2 show that, in the examples of the present invention, the tensile strength at room temperature was set in a range of 2148 to 2775 MPa, and the creep elongation was set to be 0.7 to 1.1%.

[0039] In contrast, in the case of comparative example 1 in which the Cr content was greater than that of the present invention, the tensile strength at room temperature was 1991 MPa which was lower than 93% of the examples of the present invention with the creep elongation being 1.4 times greater than that of the example of the present invention.

[0040] Moreover, in the case of comparative example 2 in which the Cr content was greater than the present invention with Mo being greater than comparative example 1, cracks occurred in cold working, making it impossible to measure the tensile strength at room temperature and creep elongation.

[0041] Furthermore, in the case of comparative example 3 in which the Cr content was greater than the present invention with the Mo content being smaller than the present invention, the tensile strength at room temperature was 1677 MPa which was lower than 78% of the examples of the present invention with the creep elongation being 1.7 times greater than that of the example of the present invention.

[0042] In the case of comparative example 4 of Inconel X750, the tensile strength at room temperature was 1451 MPa which was lower than 68% of the examples of the present invention with the creep elongation being not less than 2 times greater than that of the example of the present invention.

[0043] The results in Table 3 show that, in the case of comparative example 5 having a cold working ratio of 35%, which is lower than the cold working ratio of the example of the present invention, the tensile strength at room temperature was 1589 MPa, which was lower than that of the examples 12, 13 and 6 of the present invention, and the creep elongation was 3.8% that was greater than the examples 12, 13 and 6 of the present invention. The results of these show that the working ratio of cold working or warm working must be set to be not less than 40%.

[0044] The results in Table 4 show that, in the case of comparative example 6 having an aging treatment temperature of 450°C, which was lower than the aging temperature of the present invention, the tensile strength at room temperature was 1795 MPa, which was lower than the example of the present invention, and the creep elongation was 2.1%, which was greater than that of the present invention. Moreover, in the case of comparative example 7 having an aging treatment temperature which was higher than the aging temperature of the example of the present invention, the tensile strength at room temperature was 1314 MPa, which was lower than the example of the present invention, and the creep elongation was 4.8%, which was greater than that of the present invention.

[0045] These results show that the aging treatment temperature must be set in a range of 500 to 800°C.

[0046] As described above, the Co-Ni base heat-resistant alloy of the present invention has a higher strength at room temperature in comparison with Ni base super-heat-resistant alloys that have been conventionally used, and is less susceptible to degradation in strength even after long periods of use at high temperatures. Moreover, the preparation method of the present invention makes it possible to prepare a Co-Ni base heat-resistant alloy which has a higher strength at room temperature in comparison with Ni base super-heat-resistant alloys that have been conventionally used, and is less susceptible to degradation in strength even after long periods of use at high temperatures.

Claims

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- 1. A Co-Ni base heat-resistant alloy 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 of substantially Co and inevitable impurities.
- 10 **2.** The Co-Ni base heat-resistant alloy according to claim 1, further comprising: 0.007 to 0.10 mass% of REM.
 - 3. The Co-Ni base heat-resistant alloy according to claim 1, 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.
 - 4. The Co-Ni base heat-resistant alloy according to claim 1, further comprising: all by weight,
 - 0.007 to 0.10 mass% of REM; and 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; and 0.001 to 0.20 mass% of Zr.
 - 5. A preparation method of Co-Ni base heat-resistant alloy, the method comprising the steps of:
- subjecting an alloy which contains 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 one kind or more 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 of substantially Co and inevitable impurities, to a solid solution heat treatment at 1000 to 1200°C or a hot working at this temperature;
 - then subjecting this to a cold working or a warm working having a working ratio of not less than 40 mass%; and then subjecting this to an aging heat treatment at 500 to 800°C for 0.1 to 50 hours.
 - **6.** The preparation method of Co-Ni base heat-resistant alloy according to claim 5, wherein said alloy further comprises: 0.007 to 0.10 mass% of REM.
- **7.** The preparation method of Co-Ni base heat-resistant alloy according to claim 5, wherein said alloy further comprises: 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; and 0.001 to 0.20 mass% of Zr.
 - **8.** The preparation method of Co-Ni base heat-resistant alloy according to claim 5, wherein said alloy further comprises: all by weight,
- 0.007 to 0.10 of REM, and 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 and 0.001 to 0.20 mass% of Zr.

Fig. 1

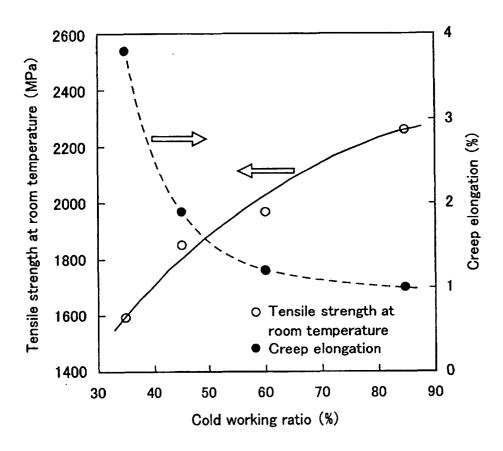
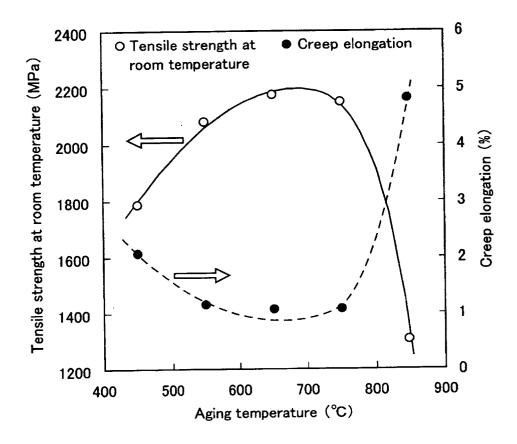


Fig. 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/08104

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C22C 19/07, C22F 1/10								
According to International Patent Classification (IPC) or to both national classification and IPC								
B. FIELDS	SEARCHED							
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ C22C 19/07, C22F 1/10								
Jits Koka	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2001 Kokai Jitsuyo Shinan Koho 1971-2001 Jitsuyo Shinan Toroku Koho 1996-2001							
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) JOIS WPI								
C. DOCUI	MENTS CONSIDERED TO BE RELEVANT							
Category*	Citation of document, with indication, where ap	· ·	Relevant to claim No.					
Х	US 5476555 A (SPS Technologies, 19 December, 1995 (19.12.95), columns 37 to 40 & JP 6-212325 A	1-8						
A	JP 63-30384 B2 (Mitsubishi Meta 17 June, 1988 (17.06.88), page 1 (Family: none)	1-8						
A	1-8							
	·							
	r documents are listed in the continuation of Box C.	See patent family annex.						
"A" docume conside "E" earlier date "L" docume	categories of cited documents: ent defining the general state of the art which is not red to be of particular relevance document but published on or after the international filing ent which may throw doubts on priority claim(s) or which is	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone						
special "O" docume means "P" docume	establish the publication date of another citation or other reason (as specified) ent referring to an oral disclosure, use, exhibition or other ent published prior to the international filing date but later	"Y" document of particular relevance; the considered to involve an inventive step combined with one or more other such combination being obvious to a person document member of the same patent if	when the document is documents, such skilled in the art					
Date of the	e priority date claimed actual completion of the international search December, 2001 (10.12.01)	Date of mailing of the international search report 18 December, 2001 (18.12.01)						
	nailing address of the ISA/ nnese Patent Office	Authorized officer						
Facsimile N	·	Telephone No.						

Form PCT/ISA/210 (second sheet) (July 1992)