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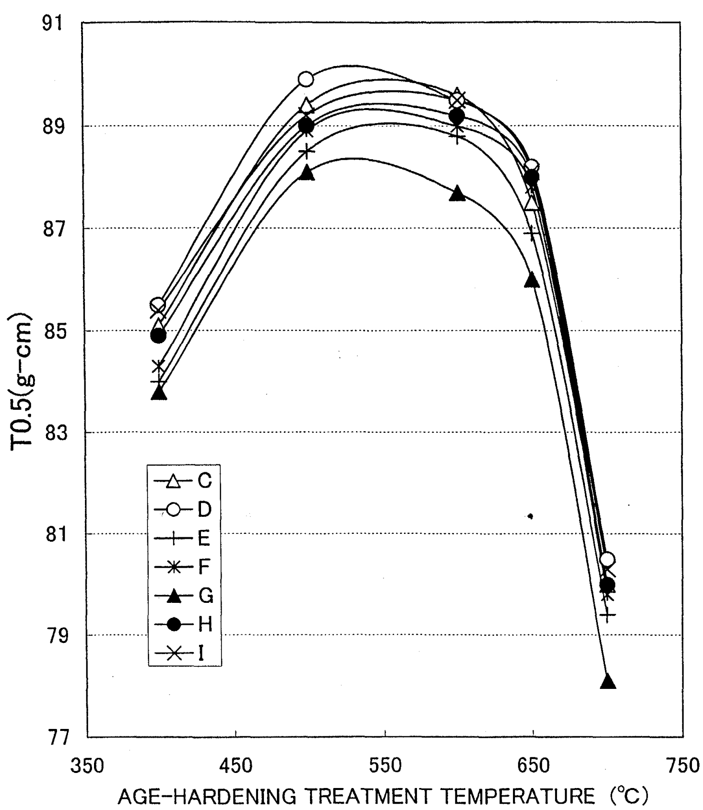
(54) Co-Ni-Base Alloy

(57) A Co-Ni-base alloy, being characterized in that a composition of the alloy comprises at least Co, Ni, Cr, Mo, W and Fe, and percentages by weight of the composition are from 25% to 45% of Co, from 25% to 40% of Ni, from 18% to 26% of Cr, from 3% to 11% of Mo, from 0.5% to 9% of W, wherein a sum of Mo and W is from 4% to 13% by weight, and from 1.1% to 5% of Fe.

Figure 6



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Description

[0001] The present invention relates to a Co-Ni-base alloy, and, more particularly to a Co-Ni-base alloy having a high elasticity and a high corrosion resistance for use in a small-size precision device and the like, a mainspring using the Co-Ni-base alloy, and a method for producing the mainspring.

[0002] To date, a Co-base alloy, a Co-Ni-base alloy which is more efficient than the Co-base alloy or the like has been used as a high elastic material for use in a small-size precision device (for example, refer to patent document 1).

[0003] Further, since a high output torque, durability and corrosion resistance are required for a mainspring of a wrist-watch, the Co-base alloy or the Co-Ni-base alloy which is high in Young's modulus or material strength, excellent in corrosion resistance and has a favorable plastic workability has been used as a material for the mainspring. The Young's modulus of the Co-base alloy which has conventionally been used in the mainspring of the wrist-watch in many occasions is in the range of from about 2.0×10^5 MPa to about 2.1×10^5 MPa. As a method for producing the mainspring of the wrist-watch which is aimed for a higher output torque than before, a method in which a Co-Ni-base alloy having a composition comprising, in terms of percentages by weight, from 30.9% to 37.2% of Co, from 31.4% to 33.4% of Ni, from 19.5% to 20.5% of Cr, from 9.5% to 10.5% of Mo, from 0.1% to 0.5% of Mn, from 0.3% to 0.7% of Ti, from 1.1% to 2.1% of Fe, from 0.8% to 1.2% of Nb, from 0.01% to 0.02% of misch metal and inevitable impurities, and having a Young's modulus of from 2.3×10^5 MPa to 2.4×10^5 MPa was prepared by vacuum melting and, then, subjected to the steps of casting, forging, hot-rolling, hot-wire-drawing, a solution treatment, cold-wire-drawing and annealing and, thereafter, subjected to a cold-wire-drawing at a final processing ratio of from 30% to 90% in terms of a reduction ratio in a cross-section area to produce a wire which was, then, cold-rolled so as to have a finishing thickness of a spring and, thereafter, subjected to an age-hardening treatment at a treatment temperature of from 400°C to 620°C for from 2 to 3 hours in a vacuum or non-oxidation atmosphere has been known (for example, refer to patent document 2).

[0004] Patent document 1: Japanese Patent No.3190566 (Pages 2 and 3); and

[0005] Patent document 2: Japanese Patent No.3041585 (Pages 2 and 3) .

[0006] Along with a performance enhancement of a small-size precision device and a severer using condition thereof, a further performance enhancement has been required for a high elastic material.

[0007] Along with a performance enhancement of a mechanical wrist-watch or a diversification of added mechanisms thereof, a higher output torque has been required for a mainspring which is an energy source, and there is a problem in that a conventional mainspring is insufficient. However, a space within the mechanical wrist-watch is limited and, accordingly, it is not advantageous to increase thickness or width of the spring.

[0008] The output torque of the mainspring is represented by the following formula:

$$T=Ebt^3\pi N/6L,$$

wherein

- T: output torque;
- E: Young's modulus of material;
- b: width of spring;
- t: thickness of spring;
- N: number of effective turns of spring; and
- L: length of spring.

[0009] As seen from the formula, a material having a high Young's modulus is necessary for obtaining a high output torque without increasing the thickness or width of the spring. Further, the mainspring of the wrist-watch is ordinarily small in size such that the thickness and width thereof are approximately 0.1 mm and 1 mm, respectively. Therefore, it is required that the material for use in the mainspring of the wrist-watch has not only a high Young's modulus, but also a favorable plastic workability property such that it can be machined into a thin narrow hoop (strip-shaped material). For this account, a material which has a high Young's modulus, a favorable plastic workability, a mainspring having a high output torque using the material and a method for producing the mainspring are required. Simultaneously, durability of the mainspring and improvement of corrosion resistance thereof are also required.

[0010] According to the present invention, an alloy in which a strengthening element is newly added to a Co-Ni-base alloy to define a composition and, as a result, mechanical strength is remarkably enhanced is provided. It has been found that, in the Co-Ni-base alloy, W alone or a combination of W and Nb was added as a strengthening element to a main elements of Co, Ni, Cr, Mo and the like to newly define a composition range thereof and, as a result, material strength was remarkably enhanced compared with an example of a conventional Co-Ni-base alloy. Further, it has been found that a mainspring having high performance can be obtained by using the Co-Ni-base alloy according to the present invention, performing plastic working so as to have a high Young's modulus in a rolling direction of such rolled material and, after working, performing an age-hardening treatment.

[0011] The Co-Ni-base alloy according to the invention has a superplastic property and is, simultaneously, imparted with a high mechanical strength, fatigue strength and an excellent corrosion resistance. A mainspring was produced by the aforementioned alloywhichhas a composition comprising at least Co, Ni, Cr, Mo, W, and Fe and percentages by weight of the composition are from 25% to 45% of Co, from 25% to 40% of Ni, from 18% to 26% of Cr, from 3% to 11% of Mo, from 0.5% to 9% of W, wherein a sum of Mo and W is from 4% to 13% by weight, and from 1.1% to 5% of Fe, and also has fine deformation twins in a parent phase. More preferably, the composition of the aforementioned alloy comprises at least one type or more of elements among Nb, Mn, B, Zr and Ti, and percentages by weight of the elements contained in the aforementioned alloy are as follows: $0 \leqq Nb \leqq 2\%$; $0 \leqq Mn \leqq 2\%$; $0 \leqq B \leqq 0.02\%$; $0 \leqq Zr \leqq 0.2\%$; and $0 \leqq Ti \leqq 1\%$.

[0012] This alloy has a favorable plastic workability and a low stacking fault energy and, accordingly, hasahigh-workhardening ability. When the alloy is subjected to cold-plastic working, fine deformation twins are densely formed in an FCC phase which is the parent phase and the like and, through a subsequent work-hardening, an alloy strength is enhanced. The cold plastic working ratio is preferably 50% or more. Further, a superplastic phenomenon is expressed by the presence of such fine deformation twins.

[0013] A method for producing a mainspring comprises the steps of : mixing elements such that a composition of an alloy comprises, in percentages by weight, from 25% to 45% of Co, from 25% to 40% of Ni, from 18% to 26% of Cr, from 3% to 11% of Mo, from 0.5% to 9% of W, wherein a sum of Mo and W is from 4% to 13% by weight, and from 1.1% to 5% of Fe and melting the alloy; subjecting the alloy to cold-wire-drawing; cold-rolling the alloy;forming the alloy; and subjecting the alloy to an age-hardening treatment.

[0014] Preferably, a processing ratio of the cold-wire-drawing is 10% or more in terms of a reduction ratio in a cross-section area. Further, the age-hardening treatment is preferably performed at a treating temperature of from 400°C to 700°C in a vacuum or non-oxidation atmosphere.

[0015] The Co-Ni-base alloy according to the present invention is enhanced in a material strength compared with the conventional Co-Ni-base alloy. For this account, it is effective to use the Co-Ni-base alloy according to the invention for the spring or the like for the precision device which requires high load, high reliability and high corrosion resistance and, therefore, it has an advantage such that it can correspond to a trend of down-sizing and being free of maintenance thereof and the like. By processing the Co-Ni-base alloy according to the invention, the mainspring having a high output torque, an excellent durability and corrosion resistance can be obtained. When the mainspring according to the invention is used as a power source of the wrist-watch, since a large driving torque can be obtained without enlarging thickness or width thereof, it is possible to increase a moment of inertial of a balance wheel, thereby being capable of decreasing a change of a rate to be caused by a vibration or a shock. Further, diversification of added mechanisms or an increase of duration period of time can be realized. Still further, even when it is repeatedlyused, since characteristics thereof are hardly deteriorated, the high output torque can be maintained. It is tough and is hardly broken. Furthermore, even when it is left in a humid environment caused by, for example, a climate, a human perspiration or the like, it performs a high corrosion resistance.

[0016] Embodiments of the present invention will now be described by way of further example only and with reference to the accompanying drawings, in which:-

Figure 1 is a table showing compositions of the Co-Ni-base alloys of Conventional Examples and Examples hereof.
Figure 2 is a table showing values of tensile strength and elongation of each of test pieces.
Figure 3 is a table showing a composition of Conventional Example d.
Figure 4 is a table showing a composition of Conventional Example e.
Figure 5 is a table showing output torque and the number of effective turns.
Figure 6 is a graph showing a relation of an age-hardening treatment temperature and torque (T 0.5) of an alloy according to the present invention.
Figure 7 is a table showing output torque and the number of effective turns.
Figure 8 is a table showing the number of repetitions to rupture.

[0017] A composition of the Co-Ni-base alloy according to the present invention comprises at least Co, Ni, Cr, Mo, W and Fe, and, in terms of percentages by weight, from 25% to 45% of Co, from 25% to 40% of Ni, from 18% to 26% of Cr, from 3% to 11% of Mo, from 0.5% to 9% of W, wherein a sum of Mo and W is from 4% to 13% by weight, and from 1.1% to 5% of Fe, and, further, has fine deformation twins in a parent phase. Preferably, the composition of the alloy comprises one type or more of elements among Nb, Mn, B, Zr and Ti, and percentages by weight of the elements contained in the alloy are as follows: $0 \leqq Nb \leqq 2$; $0 \leqq Mn \leqq 2\%$; $0 \leqq B \leqq 0.02\%$; $0 \leqq Zr \leqq 0.2\%$; and $0 \leqq Ti \leqq 1\%$. A mainspring is produced from the Co-Ni-base alloy having the aforementioned composition.

[0018] Since the alloy which is a material of the mainspring according to the invention has a favorable plastic workability and has a low stacking fault energy, it has a high work-hardening ability. When it is subjected to cold-plastic working, fine deformation twins are densely formed in an FCC phase or the like and, accordingly, work-hardened, thereby enhancing the alloy strength thereof. When the mainspring is produced by using an alloy which is added with W alone or a combination of W and Nb as a strengthening element, the mainspring having a high torque can be obtained.

[0019] This alloy is strengthened by solid-solution Mo in the parent phase which is the FCC phase, and a stacking fault energy is decreased thereby a high work-hardening ability appears by solid-solution Cr and, further, the parent phase is more strengthened by solid-solution W. Still further, when it is subjected to cold plastic working, fine deformation twins are densely formed in the parent phase and, also, solute atoms are segregated in the stacking fault and, therefore, dislocation motions are blocked and, accordingly, work-hardened, thereby enhancing the alloy strength. When it is subjected to an age-hardening treatment in a work-hardened state, the solute atoms are segregated in the stacking fault to fix such dislocation. That is, the alloy strength is further enhanced by so-called strain age-hardening. Addition of Nb enhances strain age-hardening ability. By enhancing the strength in such a manner as described above, tensile strength, yield-strength and Young's modulus are enhanced and, therefore, when the mainspring is produced by using this alloy, the mainspring having a high output torque and an excellent durability can be obtained.

[0020] This alloy is prepared by vacuum melting and, then, subjected to the steps of casting, forging, hot-rolling, hot-wire-drawing, a solution treatment, cold-wire-drawing, and annealing and, thereafter, subjected to cold-wire-drawing at a processing ratio of 10% or more in terms of a reduction ratio in a cross-section area. Since this alloy has a relatively large deformation resistance, it is preferable to perform wire-drawing by using a back-tensioning wire-drawing machine. A wire obtained by such performance is cold-rolled without being subjected to annealing until thickness thereof comes to a finishing thickness of the spring.

[0021] The reason why it is subjected to rolling after subjected to wire-drawing is that Young's modulus in a rolling direction of the thus-rolled material becomes higher than that of the rolled material which has been subjected to rolling without being subjected to the wire-drawing and, accordingly, an output torque of the mainspring can be enhanced. The reason why the processing ratio of the wire-drawing is set to be 10% or more is that 10% is a lower limit that an effect of enhancing Young's modulus in the rolling direction of the rolled material appears. Further, when the cold-plastic working is performed in such manner as described above, fine deformation twins are densely formed in the parent phase which is a texture of the rolled material and the like and, accordingly, it is work-hardened, thereby enhancing the strength. This rolled material is cut so as to have a width corresponding to a finishing width of the spring, subjected to edge polishing to form a hoop having a rounded corner. Thus-formed hoop is subjected to the steps of sizing, forming, welding, an age-hardening treatment, and a surface treatment to produce the mainspring. The age-hardening treatment is performed at a temperature of from 400°C to 700°C for from one to 10 hours in a vacuum or non-oxidation atmosphere. By such performance, the mainspring is strain-age-hardened to further enhance the strength. In a manner as described above, the mainspring having a high output torque and excellent durability and toughness can be obtained.

[0022] Next, a reason why the composition range is defined is described. The reason why Co and Ni are defined to be in the ranges of from 25% to 45% and from 25% to 40%, respectively, is that these ranges are optimal ones for forming a consistent FCC phase, obtaining a favorable plastic workability and a high work-hardening ability. The reason why Cr is defined to be in the range of from 18% to 26% is that 18% or more is desirable to obtain an excellent corrosion resistance and a high work-hardening ability, while, when Cr is over 26%, a σ phase is precipitated to cause a risk for allowing the mainspring to become brittle.

[0023] Next, a reason why Mo and W are defined is described. Mo and W are elements which most contribute to solid-solution hardning of the FCC phase. In a composition in which Co, Ni, and Cr are contained in the aforementioned ranges, respectively, the ranges in which Mo is from 3% to 11% and W is from 0.5% to 9%, wherein a sum of Mo and W is 4% or more by weight are appropriate ones for solid-solution strengthening of the FCC phase. However, when the sum of the percentages by weight of Mo and W is unduly large, the σ phase is precipitated to cause a risk of allowing the mainspring to become brittle. For this account, it is optimal for obtaining the mainspring having a high output torque and an excellent toughness that Mo and W are in the aforementioned ranges, respectively, wherein the sum of the percentages by weight of Mo and W is in the range of from 4% to 13% by weight

[0024] Next, a reason for defining $0 \leqq Nb \leqq 2\%$ is described. This alloy may be added with either W alone, or a combination of WandNb. Nb not only enhances the strain age-hardening ability, but also combines with C to form a carbide which is precipitated in a crystal grain boundary to contribute to suppressing crystal grains form becoming rough and large or strengthening the grain boundary. In such manner as described above, Nb contributes to enhancing the characteristics of the alloy for themainspring. However, when Nb is over 2% by weight, a δ phase is generated to deteriorate the characteristics of the alloy for the mainspring. For this account, by defining the percentages by weight of Nb as being in $0 \leqq Nb \leqq 2\%$, the δ phase is not precipitated and,accordingly,afavorable plastic workabilityismaintained and strength after subjected to the age-hardening treatment is enhanced, thereby enhancing the output torque of the mainspring. Further, when a combination of W and Nb is added, as a result, an amount of W can be smaller than that in a case in which W is added alone and, therefore, a growth of dendrite of a cast texture can be suppressed, thereby enhancing forging workability.

[0025] A reason why Fe is defined to be in the range of from 1.1% to 5% is that the range is an optimal one for solid-hardening the FCC phase without deteriorating oxidation resistance. Mn is effective in cleaning the alloy as a deoxidant or a desulfurigation element, and is effecive in enhancing work-hardening ability caused by decreasing a stacking fault energy. However, when an amount thereof is unduly large, corrosion resistance become deteriorated. For this account, an optimal range of Mn is $0 \leqq Mn \leqq 2\%$ by weight. B is effective in enhancing strength of the crystal grain boundary to enhance workability; however, when an amount thereof is unduly large, workability is deteriorated to the contrary. For this account, an optimal range of B is $0 \leqq B \leqq 0.02\%$ by weight. Zr is effective in enhancing the strength of the crystal grain boundary at an elevated temperature to enhance hot-workability; however, when an amount of Zr is unduly large, workability is deteriorated to the contrary. For this account, an optimal range of Zr is $0 \leqq Zr \leqq 0.2\%$ by weight. Ti has, as a deoxidant, effects in cleaning the alloy and suppressing the crystal grain from becoming rough and large; however, when an amount of Ti is unduly large, a η phase is formed to hinder the workability. For this account, an optimal range of Ti is $0 \leqq Ti \leqq 1\%$ by weight.

[0026] Hereinafter, embodiments are described. In Figure 1, compositions of the Co-Ni-base alloys of Conventional Examples and Examples according to the invention are shown in terms of percentages by weight. These alloys were melted in a vacuum melting furnace and, then, cast. Each of the resultant alloy ingots was forged, hot-rolled and, then, cold-rolled to produce a rolled material having a thickness of 0.5 mm by means of cold-rolling reduction ratios of 50% and 75%. Test pieces were prepared in accordance with JIS specifications by using the thus-produced rolled material. The thus-prepared test pieces were each subj ected to an age-hardening treatment for two hours at a temperature of from 200°C to 1000°C in a vacuum heat- treating furnace. The resultant test pieces were each subjected to a tensile test. In Figure 2, shown are values of tensile strength σ_B (MPa) and elongation ε (%) of each of test pieces which have been subjected only up to such cold-processing and those which have further been subjected to the age-hardening treatment: 500°C×2 hours.

[0027] As is seen from Figure 2, in the Co-Ni -base alloys according to the present invention (Examples 1 to 7) , the tensile strength after the age-hardening treatment of 500°C×2 hours shows higher values by from about 12% to 15% compared with those of the conventional Co-Ni-base alloys (Conventional Examples a to c) . Namely, it is found that material strength has been enhanced as an effect of adding W into the alloy composition.

[0028] Mainsprings of the wrist-watches were produced by using an example of the Co-Ni-base alloy (Conventional Example d) for use in the conventional mainspring, another example of the Co-Ni-base alloy (Conventional Example e) for use in the conventional mainspring, and examples of alloys (Examples 1 to 7) each for use in the mainspring according to the present invention to compare spring characteristics thereamong. In Figures 3 and 4, shown are compositions of these alloys employed in Conventional Example d and Conventional Example e, respectively.

[0029] Each of the above-described alloys was prepared by using a vacuum melting furnace and, then, subjected to the steps of casting, forging, hot-rolling, hot-wire-drawing, a solution treatment, cold-wire-drawing, andannealingand, subsequently, subject to wire-drawing of 60% in terms of a reduction ratio in a cross-section area at room temperature by using a back-tensioning wire-drawing machine, thereby producing a wire having a diameter of 3 mm. The thus-produced wire was rolled until it had a finishing thickness of a mainspring and, then, cut widthwise so as to have a spring finishing width to produce a hoop having a thickness of 0.12 mm and a width of 0.95 mm and, thereafter, an edge portion of the thus-produced hoop was subjected to polishing. Subsequently, the resultant hoop was cut to have a length of 370 mm and, then, a leading-end portion thereof was provided with a square hole and formed and, thereafter, a trailing-end thereof was welded with an outer hooking part. Thereafter, the resultant hoop was subjected to the age-hardening treatment at each of 400°C, 500°C, 600°C, 650°C and 700°C for 2 hours in a vacuum atmosphere and, lastly, a surface treatment was performed such that TEFLON was applied thereto. In such a manner as described above, each of mainsprings was produced. The mainspring was inserted in a barrel and, then, spring characteristics were examined. An inner diameter of the barrel and a winding-core diameter were 10.60 mm and 2.80 mm, respectively.

[0030] In Figure 5, in regard to Conventional Example d, Conventional Example e and Examples 1 to 7 according to the present invention which each have been subjected to an age-hardening treatment at 500°C, T 0.5 (output torque in a state in which a portion of the mainspring corresponding to 0.5 hour was unwound after fully wound up) , T 24 (output torque in a state in which a portion of the mainspring corresponding to 24 hours was unwound), and the number of effective turns N of the spring which is related with a duration period are shown. In Figure 6, shown is a graph illustrating a relation between an age-hardening treatment temperature and T 0.5.

[0031] As is seen from Figure 5, Examples according to the present invention each have a higher output torque by about 33% in T 0.5 and by about 38% in T 24 than that of Conventional Example d and by about 15% in T 0.5 and by about 17% in T 24 than that of Conventional Example e. In a case in which the output torques of Examples and Conventional Examples are allowed to be same with each other, since thickness of the spring of Examples according to the present invention can be smaller than those of Conventional Example d and Conventional Example e, the number of effective turns N of the spring can be increased in a limited space and, accordingly, the duration period of time of the wrist-watch can be expanded. Further, as is seen from Figure 6 , T0.5 of each Example according to the invention canbe enhanced by performing the age-hardening treatment in the temperature range of from 400°C to 700°C, and T 0.5 becomes maximum in the range of from 500°C to 600°C.

[0032] Next, a spring endurance test (acceleration test of fully-wound- fully-unwound repetition) was conducted to examine an output torque and the number of turns and the number of repetitions which reached a rapture after 500 repetitions. In Figure7, in regard to Conventional Example d and Conventional Example e, Examples 1 and 2 as being representative of Examples according to the invention, the output torque and the number of turns after 500 repetitions in a case of being subjected to the age-hardening treatment at 500°C for 2 hours are shown, while, in Figure 8, the number of repetitions which reached a rapture is shown. It is found that Examples according to the invention are each small in torque deterioration or decrease in the number of turns to be caused by fatigue of the spring generated by being subjected to a 500-time repetition, and are each equivalent or higher in the number of repetitions which reached a rapture, and are, also, excellent in durability, compared with Conventional Example d and Conventional Example e.

[0033] Further, Examples of the mainspring according to the invention have described only about manually wound mainsprings; however, similar excellent spring characteristics can be obtained also in automatically wound mainsprings. Further, since the mainspring according to the invention contains a large amount of elements such as Cr and the like which enhance the corrosion resistance and a small amount of Fe, it has an extremely favorable corrosion resistance and, when it was subjected to an immersion test in artificial human perspiration and a salt water spray test, stain or discoloration was not generated.

[0034] It will be obvious to those having skill in the art that many changes may be made in the above-described details of the preferred embodiments of the present invention. The scope of the present invention, therefore, should be determined by the following claims.

Claims

1. A Co-Ni-base alloy, being **characterized in that** a composition of the alloy comprises at least Co, Ni, Cr, Mo, W and Fe, and percentages by weight of the composition are from 25% to 45% of Co, from 25% to 40% of Ni, from 18% to 26% of Cr, from 3% to 11% of Mo, from 0.5% to 9% of W, wherein a sum of Mo and W is from 4% to 13% by weight, and from 1.1% to 5% of Fe.

2. The Co-Ni-base alloy as set forth in Claim 1, being **characterized in that** the composition of the alloy comprises one type or more of elements among Nb, Mn, B, Zr and Ti, and percentages by weight of the elements contained in the alloy are as follows:

$$0 \leqq Nb \leqq 2\%,;\ 0 \leqq Mn \leqq 2\%;\ 0 \leqq B \leqq 0.02\%;\ 0 \leqq Zr \leqq 0.2\%;\ \text{and}\ 0 \leqq Ti \leqq 1\%.$$

3. The Co-Ni-base alloy as set forth in Claim 1 or 2, being **characterized by** having been subjected to cold-plastic working.

4. The Co-Ni-base alloy as set forth in Claim 3, being **characterized in that** a processing ratio of the cold-plastic working is 50% or more.

5. The Co-Ni-base alloy as set forth in any one of Claims 1, and 2, being **characterized by** having been subjected to an age-hardening treatment.

6. The Co-Ni-base alloy as set forth in Claim 5, being **characterized in that** a temperature of the age-hardening treatment is from 200°C to 700°C.

7. The Co-Ni-base alloy as set forth in any one of Claims 1 and 2 being **characterized by** having fine deformation twins in a parent phase.

8. A mainspring, being **characterized by** comprising the Co-Ni-base alloy as set forth in any one of Claims 1 and 2.

9. A method for producing a mainspring comprising the steps of:

   mixing elements such that a composition of an alloy comprises, in terms of percentages by weight, from 25% to 45% of Co, from 25% to 40% of Ni, from 18% to 26% of Cr, from 3% to 11% of Mo, from 0.5% to 9% of W, wherein a sum of Mo and W is from 4% to 13% by weight, and from 1.1% to 5% of Fe and melting the alloy;

subjecting the alloy to cold-wire-drawing;
cold-rolling the alloy;
forming the alloy; and
subjecting the alloy to an age-hardening treatment.

10. The method for producing the mainspring as set forth in Claim 9, being **characterized in that** a processing ratio of the cold-wire-drawing is 10% or more in terms of a reduction ratio in a cross-section area.

11. The method for producing the mainspring as set forth in Claim 9, being **characterized by** performing the age-hardening treatment at a treating temperature of from 400°C to 700°C in a vacuum or non-oxidation atmosphere.

Figure 1

	Mn	Ni	Cr	Mo	W	Nb	Fe	Ti	B	Zr	M.M.	Co
Conventional Example a	0.3	26.2	24.8	9.1	-	1.3	1.8	0.6	0.01	-	0.01	35.88
Conventional Example b	0.2	31.7	23.7	11.8	-	1	2.6	0.5	0.01	-	0.01	28.48
Conventional Example c	0.2	40.4	18.2	8	-	2	1.7	0.5	0.01	-	0.01	28.98
Example 1	0.8	35.4	20.2	7.2	4.9	-	2.1	0.5	-	0.12	-	28.78
Example 2	0.4	33.1	24.1	6.1	3	1.4	1.8	-	0.01	0.05	-	30.04
Example 3	0.2	32.8	19.5	10.5	0.6	0.6	4.6	0.4	0.01	-	-	30.79
Example 4	0.8	38	21.8	3.9	8.2	-	1.3	0.5	-	0.15	-	25.35
Example 5	1.5	29.6	18.8	8	0.8	1	1.5	-	0.015	-	-	38.075
Example 6	1.1	26.2	18	3	1.1	2	3.5	0.6	0.01	-	-	44.49
Example 7	0.3	28	24.7	6.8	2	1.2	3	-	0.01	0.1	-	33.89

M.M.: misch metal

Figure 2

	After cold-rolling				After age-hardening treatment: 500°Cx2hrs.			
Reduction ratio	50%		75%		50%		75%	
Characteristics	σ_B (MPa)	ε (%)	σ_B (MPa)	ε (%)	σ_B (MPa)	ε (%)	σ_B (MPa)	ε (%)
Conventional Example a	1830	8.2	2156	10.5	2096	4	2565	6.3
Conventional Example b	1841	7.9	2172	9.8	2099	4	2585	6.5
Conventional Example c	1799	8.8	2139	10.4	2069	4.5	2524	6.7
Example 1	1917	11.8	2215	10.6	2258	6.5	2877	7.2
Example 2	2042	12.2	2312	11.1	2402	6.9	3003	7.6
Example 3	1900	11.3	2200	10.2	2289	6.1	2935	6.9
Example 4	1962	12	2245	10.8	2364	6.3	2918	7.3
Example 5	1939	12.4	2199	11	2255	6	2892	6.7
Example 6	2089	12.8	2277	11.3	2487	7	2996	7.7
Example 7	2025	11.9	2371	10.8	2408	7	3011	7.8

Figure 3

(weight %)

	Si	Mn	Co	Ni	Cr	Mo	W	Ti	Al	Fe
Conventional Example d	0.9	0.6	38.9	16.5	11.9	4.1	4	0.6	0.08	22.42

Figure 4

(weight %)

	Mn	Ni	Cr	Mo	Nb	Fe	Ti	M.M.	Co
Conventional Example e	0.3	32.4	20.1	9.9	1	2	0.4	0.01	33.89

M.M.: misch metal

Figure 6

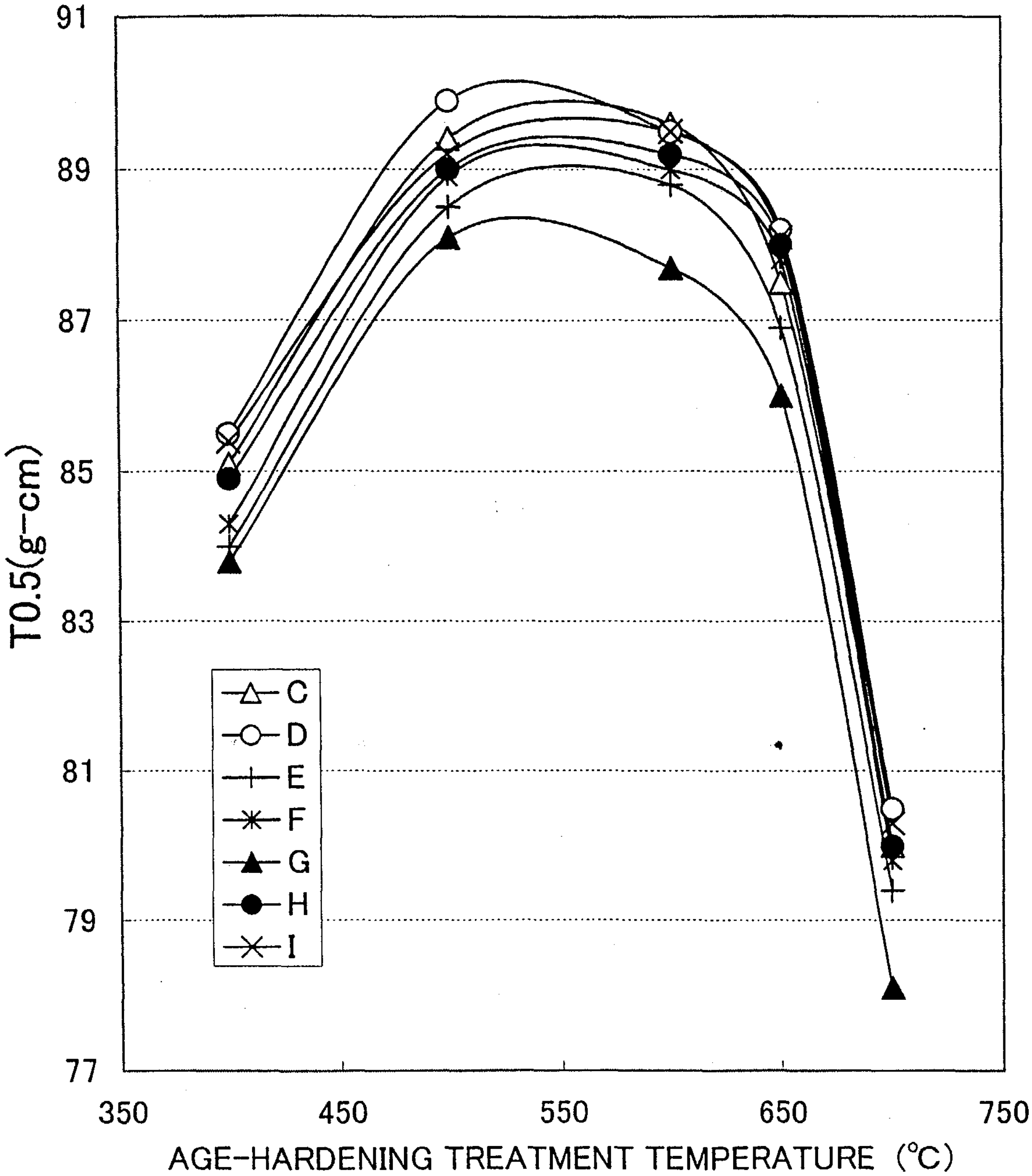
91
89
87
85
83
81
79
77
T0.5(g-cm)
C
D
E
F
G
H
I
350
450
550
650
750
AGE-HARDENING TREATMENT TEMPERATURE (°C)

Figure 5

	T 0.5 (g-cm)	T 24 (g-cm)	N (number of effective turns)
Conventional Example d	66.9	53.8	6.8
Conventional Example e	77.2	63.5	7
Example 1	89.4	74.4	7.2
Example 2	89.9	74.8	7.2
Example 3	88.5	73.6	7.1
Example 4	88.9	74	7.1
Example 5	88.1	73.2	7.1
Example 6	89	74.3	7.1
Example 7	89.2	74.7	7.2

Figure 7

	T 0.5 (g-cm)	T 24 (g-cm)	N (number of effective turns)
Conventional Example d	59.5	48.4	6.2
Conventional Example e	73.3	61	6.6
Example 1	85.8	72	6.9
Example 2	86.2	72.3	6.9

Figure 8

	Number of repetitions reaching rupture (number)
Conventional Example d	1128
Conventional Example e	1392
Example 1	1388
Example 2	1320

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EUROPEAN SEARCH REPORT

Application Number
EP 04 25 1115

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 Y	US 2002/155025 A1 (DAUM WOLFGANG) 24 October 2002 (2002-10-24) * paragraphs [0003],[0004]; claims 1,2 *	1,2,5,8 3,4,6,7, 9-11	C22C19/00
Y,D	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 05, 30 May 1997 (1997-05-30) & JP 09 013136 A (SEIKO INSTR INC), 14 January 1997 (1997-01-14) * abstract *	3,4,6,7, 9-11	
X	EP 1 154 027 A (SUMITOMO ELECTRIC INDUSTRIES) 14 November 2001 (2001-11-14) * paragraphs [0011],[0015],[0029]; claim 1 *	1-11	
D,A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 03, 31 March 1997 (1997-03-31) & JP 08 311587 A (SEIKO INSTR INC), 26 November 1996 (1996-11-26) * abstract *	1-11	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C22C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	22 June 2004	Rolle, S

CATEGORY OF CITED DOCUMENTS

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22-06-2004

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002155025 A1	24-10-2002	DE 10108581 A1	05-09-2002
JP 09013136 A	14-01-1997	JP 3041585 B2	15-05-2000
EP 1154027 A	14-11-2001	BR 0006970 A	12-06-2001
		EP 1154027 A1	14-11-2001
		JP 3371423 B2	27-01-2003
		US 6478897 B1	12-11-2002
		CN 1101479 B	12-02-2003
		WO 0044950 A1	03-08-2000
		TW 491899 B	21-06-2002
JP 08311587 A	26-11-1996	JP 3190566 B2	23-07-2001

EPO FORM P0459

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