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

(11) EP 2 868 758 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
06.05.2015 Bulletin 2015/19

(21) Application number: 13813342.6

(22) Date of filing: 02.07.2013

(51) Int Cl.:
C22C 9/00 (2006.01) *C22F 1/08* (2006.01)
H01B 1/02 (2006.01) *H01B 5/02* (2006.01)
H01B 13/00 (2006.01) *C22F 1/00* (2006.01)

(86) International application number:
PCT/JP2013/068160

(87) International publication number:
WO 2014/007259 (09.01.2014 Gazette 2014/02)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(30) Priority: 02.07.2012 JP 2012148920

(71) Applicant: Furukawa Electric Co., Ltd.
Chiyoda-ku
Tokyo 100-8322 (JP)

(72) Inventor: TAKAZAWA, Tsukasa
Tokyo 100-8322 (JP)

(74) Representative: Forstmeyer, Dietmar et al
BOETERS & LIECK
Oberanger 32
80331 München (DE)

(54) COPPER-ALLOY WIRE ROD AND MANUFACTURING METHOD THEREFOR

(57) {Problem to solve} To provide, at low cost, a copper alloy wire that is excellent in elongation, and resistance to bending fatigue, and that can be suitable for the use in, for example, magnet wires.

{Means to solve} A copper alloy wire, having an alloy composition containing 0.5 to 4 mass% of Ag, and at least one selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr each at a content of 0.05 to 0.3 mass%, with the balance being Cu and unavoidable impurities, wherein the copper alloy wire has a wire diameter or a wire thickness of 0.1 mm or less, and wherein the nanoindentation hardness in a depth region extending from the outermost surface of the wire toward at least 5% inner side in the wire diameter or the wire thickness is 1.45 GPa or more, the nanoindentation hardness at the center of the wire is less than 1.45 GPa, the tensile strength of the wire is 350 MPa or more, and the elongation of the wire is 7% or more; and a method of producing the copper alloy wire.

EP 2 868 758 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to a copper alloy wire and a method of producing the same, and more specifically the present invention relates to an extra-fine copper alloy wire for magnet wires and a method of producing the same.

BACKGROUND ART

[0002] Along with the development in electronic equipment, making the size of an electronic part smaller is in progress, and there is an increasing demand for extra-fine copper alloy wire (round wire) having a wire diameter of 0.1 mm or less. For example, a coil for micro speakers that is used in mobile phones, smart phones, and the like, is produced by working an extra-fine wire (a magnet wire) having a wire diameter of 0.1 mm or less by winding into a coil shape.

[0003] For this winding, toughness (elongation) is required as the workability capable of turn formation, and pure copper excellent in toughness has been conventionally used. However, although pure copper is excellent in electrical conductivity, due to its low physical strength, there is a problem that pure copper is low in resistance to fatigue that is accompanied by coil vibration.

[0004] In order to solve this problem, there is a proposal of a technique of using a high-concentration Cu-Ag alloy containing 2 to 15 mass% of Ag that can enhance the tensile strength almost without lowering the electrical conductivity (Patent Literature 1). Furthermore, in general, a metal or an alloy, which has been subjected to working, is enhanced in tensile strength and lowered in elongation; however, when this is subjected to heating at a certain temperature or higher, elongation is recovered again, while physical strength is lowered. Thus, there is a proposal of a technique of achieving a balance between physical strength and elongation even in a low-concentration alloy, by carrying out the heating at a temperature lower than or equal to the softening temperature (Patent Literature 2). Furthermore, there is a proposal of a technology of enhancing resistance to bending fatigue, by applying compressive stress by subjecting a soft copper alloy wire with diameter ϕ2.6 mm and with electrical conductivity 98%IACS or more, to surface working (Patent Literature 3).

CITATION LIST

PATENT LITERATURES

[0005]

Patent Literature 1: JP-A-2009-280860 ("JP-A" means unexamined published Japanese patent application)
Patent Literature 2: Japanese Patent No. 3941304
Patent Literature 3: JP-A-05-86445

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0006] However, according to the demand for lengthening the service life of magnet wires and the demand for making magnet wires finer (with a wire diameter of 0.08 mm or less) as a result of making the size of electronic parts further smaller, further enhancement of resistance to bending fatigue and further strength enhancement of copper alloy wires has been demanded. As described in Patent Literature 1, when the Ag content is increased in order to further increase the physical strength, rather, electrical conductivity is lowered. Furthermore, since Ag is highly expensive, a noticeable increase in the cost is brought about. Furthermore, it is difficult to achieve further enhancement in physical strength and enhancement of resistance to bending fatigue, while securing electrical conductivity and elongation, using the conventional general solid solution-type highly electronic conductive copper alloy wire, as described in Patent Literature 2. Moreover, when it is intended to perform surface working so that the technology of Patent Literature 3 can be applied to a soft copper wire or copper alloy wire having a diameter of ϕ0.1 mm or less, since the soft copper wire or copper alloy wire having a diameter of ϕ0.1 mm or less has a markedly smaller wire diameter than the copper alloy wire described in Patent Literature 3, the strength of the copper alloy wire itself is low, and wire breakage occurs due to the load at the time of working, so that working itself is difficult to conduct.

[0007] Furthermore, recently, the shape of magnet wires is not limited to round wires, and investigations have also been conducted on the employment of square wires and rectangular wires. Even in the cases of these square wires and rectangular wires, it is requested to employ a wire with a thickness that is thin to the extent of that corresponding to the wire diameter of the round wire.

[0008] The present invention was achieved in view of the problems in those conventional art, and it is an object of the present invention to provide, at low cost, a copper alloy wire that is excellent in elongation, and resistance to bending fatigue, and that can be suitable for the use in, for example, magnet wires.

SOLUTION TO PROBLEM

[0009] The inventors of the present invention conducted thorough investigations on various copper alloys, and heating and working conditions therefor, in order to develop a copper alloy wire that is superior in elongation, and resistance to bending fatigue, and that is suitably used in magnet wires, and the like. As a result, the inventors have found that when a copper alloy wire having a predetermined alloy composition is subjected to a semi-softening treatment, then the wire surface section is subjected to cold-working at a certain light working ratio, and thereby the hardness is increased to a predetermined level in a certain shallow range from the surface of the wire, a copper alloy wire having excellent elongation and resistance to bending fatigue can be obtained. The present invention was completed based on those findings.

[0010] That is, the present invention provides the following means:

(1) A copper alloy wire, having an alloy composition containing 0.5 to 4 mass% of Ag, and at least one selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr each at a content of 0.05 to 0.3 mass%, with the balance being Cu and unavoidable impurities, wherein the copper alloy wire has a wire diameter (in the case of a round wire) or a wire thickness (in the case of a square wire or a rectangular wire) of 0.1 mm or less, wherein the nanoindentation hardness in a depth region extending from the outermost surface of the wire toward at least 5% inner side in the wire diameter or the wire thickness is 1.45 GPa or more, the nanoindentation hardness at the center of the wire is less than 1.45 GPa, the tensile strength of the wire is 350 MPa or more, and the elongation is 7% or more.
(2) The copper alloy wire according to (1), wherein Ag is contained in an amount of 0.5 to 4.0 mass%.
(3) The copper alloy wire according to (1), wherein at least one selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr is contained in an amount of the respective alloying element of 0.05 to 0.3 mass%.
(4) A method of producing a copper alloy wire, containing the steps of:

wire-working of subjecting a rough-drawn wire of a copper alloy having an alloy composition containing 0.5 to 4 mass% of Ag, and at least one selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr each at a content of 0.05 to 0.3 mass%, with the balance being Cu and unavoidable impurities, to cold-working, to form a wire having a wire diameter or a wire thickness of 0.1 mm or less;
final-heating of subjecting the wire to heating so as to allow the wire after the heating to have a tensile strength of 330 MPa or more and an elongation of 10% or more; and
cold-working the wire that has been subjected to the heating, at a working ratio of 3 to 15%,
wherein the nanoindentation hardness in a depth region extending from the outermost surface of the wire toward at least 5% inner side in the wire diameter or the wire thickness is 1.45 GPa or more, the nanoindentation hardness at the center of the wire is less than 1.45 GPa, the tensile strength of the wire is 350 MPa or more, and the elongation is 7% or more.

(5) The method of producing a copper alloy wire according to (4), wherein in the wire-working step, intermediate heating is carried out in the course of a plurality of cold-working steps so that the wire after this intermediate heating would have a tensile strength of 330 MPa or more and an elongation of 10% or more.

[0011] Herein, in the present specification, a semi-softened state means a state in which elongation of the copper alloy wire satisfies 10% or more, preferably 10% to 30%. Also, a semi-softening treatment means a heating that brings about the semi-softened state. On the other hand, a softened state means a recovered state in which elongation of a copper alloy wire is more than 30%. Furthermore, a softening treatment means a heating at a high temperature that brings about the softened state.

[0012] In the present invention, a wire means to include a square wire or a rectangular wire, in addition to a round wire. Thus, unless otherwise specified, the wire of the present invention collectively means a round wire, a square wire, and a rectangular wire. Herein, the size of the wire means, in the case of a round wire (the cross-section in the transverse direction (TD) is circular), the wire diameter φ (the diameter of the circle of the cross-section) of the round wire; in the case of a square wire (the cross-section in the transverse direction is square), the thickness t and the width w (each being the length of one side of the square of the cross-section and being identical to each other) of the square wire; and in the case of a rectangular wire (the cross-section in the transverse direction is rectangular), the thickness t (the length of a shorter side of the rectangle of the cross-section) and the width w (the length of a longer side of the rectangle of the cross-section) of the rectangular wire.

ADVANTAGEOUS EFFECTS OF INVENTION

[0013] Since the copper alloy wire of the present invention is excellent in resistance to bending fatigue, while having elongation necessary in coil-formation, the wire is preferably suitable as, for example, a copper alloy wire for magnet wires. Also, the method of producing the copper alloy wire of the present invention is preferably suitable as the producing method of the copper alloy wire, which is excellent in the performance.

BRIEF DESCRIPTION OF DRAWING

[0014]

{Fig. 1}
Fig. 1 is a front view schematically showing the apparatus used in the test for measuring the number of repeating times at breakage in bending fatigue (the number of repeating times at breakage), which was conducted in the Examples.

MODE FOR CARRYING OUT THE INVENTION

[0015] The present invention will be described in detail below.

[Hardness at surface portion of wire]

[0016] In regard to the copper alloy wire of the present invention, the nanoindentation hardness in a depth region extending from the outermost surface of the wire toward at least 5% inner side of the wire diameter in the case of a round wire, or of the wire thickness in the case of a square wire or a rectangular wire, is 1.45 GPa or more. According to the present invention, the nanoindentation hardness in a depth region extending from the outermost surface of the wire toward 20% inner side at the maximum of the wire diameter or the wire thickness, can be adjusted to 1.45 GPa or more. Preferably, the nanoindentation hardness in a depth region extending from the outermost surface of the wire toward 15% inner side of the wire diameter or the wire thickness, is adjusted to 1.45 GPa or more. Herein, the region having the particular nanoindentation hardness is formed to acquire the hardness, by work hardening with a final (finish) working that is provided after the final heating resulting in a semi-softened state. In the present specification, the particular depth region of the wire surface formed by such working is also referred to as "surface worked layer" or "wire surface section". Also, the center of the wire has a nanoindentation hardness of less than 1.45 GPa, and the wire as a whole is not hardened like the wire surface section. According to the present invention, the reason why the region having a nanoindentation hardness of 1.45 GPa or more is set to extend from the outermost surface of the wire toward 20% inner side at the maximum of the wire diameter or the wire thickness, is that if the wire is hardened to a deeper region beyond this range (toward the center side of the wire), elongation cannot be sufficiently secured.

[0017] Furthermore, on the side closer to the center than this surface worked layer, the wire is in the semi-softened state as a result of the final heating and is not hardened. The nanoindentation hardness on the inner side than the surface worked layer (representatively, the central section of the wire) is usually less than 1.45 GPa, and in order to sufficiently secure elongation, the nanoindentation hardness is preferably 1.3 GPa or less.

[0018] Herein, the nanoindentation hardness means the hardness that can be determined by a method for measuring the hardness of a microscopic region, which is called a nanoindentation method, by pressing a triangular pyramid diamond indenter against the surface of a (wire) sample, and determining the hardness from the load exerted at that time and the contact projection area between the indenter and the sample. Between the nanoindentation hardness and the Vickers hardness, which is a general index of hardness, for example, the relationship of Vickers hardness = (76.2 × nanoindentation hardness) + 6.3 is known (Non-Patent Literature 1).

[0019] Non-Patent Literature 1: Kinzoku (Metal), Vol. 78 (2008) No. 9, p. 47

[0020] In regard to the copper alloy wire of the present invention, the wire surface section is formed as a work-hardened surface worked layer, and the resistance to bending fatigue of the wire can be further enhanced by adjusting the nanoindentation hardness at this wire surface section preferably to 1.5 GPa or more. Furthermore, when the thickness of the surface worked layer in which this predetermined nanoindentation hardness is 1.5 GPa or more is a depth region extending from the outermost surface of the wire toward at least 5% inner side of the wire diameter or the wire thickness (a depth region extending toward 20% inner side at the maximum, and preferably a depth region extending toward 15% inner side), satisfactory characteristics, such as an elongation of 10% or more, for the copper alloy wire as a whole can be exhibited. Therefore, an excellent magnet wire can be obtained.

[0021] In regard to the copper alloy wire of the present invention, the nanoindentation hardness at the wire surface section is set to 1.45 GPa or more; however, it is more preferable to set the nanoindentation hardness to 1.6 GPa or more. The upper limit is not particularly limited, but is usually set to 1.7 GPa or less.

[Alloy composition]

[0022] The copper alloy wire of the present invention contains (i) Ag at a content of 0.5 to 4 mass%, and/or (ii) at least one selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr each at a content of 0.05 to 0.3 mass%, with the balance being Cu and unavoidable impurities. Herein, when the content of an alloy additive element is simply expressed in "percent (%)", this means "mass%". Also, there are no particular limitations on the total content of at least one alloy component selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr; however, in order to prevent a noticeable decrease in the electrical conductivity of the copper alloy wire, the total content of at least one alloy component selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr, in addition to Ag, is preferably 0.5 mass% or less.
[0023] The copper alloy wire of the present invention may contain (i) Ag alone, or may contain (ii) at least one selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr alone, or may contain both (i) Ag and (ii) at least one selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr.
[0024] These elements each are a solid solution strengthening-type or precipitation strengthening-type element, and when any of these elements is/are added to Cu, physical strength can be enhanced without lowering the electrical conductivity to a large extent. As a result of this addition, the physical strength of the copper alloy wire itself is enhanced, and the resistance to bending fatigue is enhanced. Also, even if the wire is worked into an extra-fine wire having a wire diameter or a wire thickness of 0.1 mm or less, followed by subjecting to a heating (semi-softening treatment), since the wire surface section is hardened after the semi-softening treatment, the wire can withstand the final (finish) cold-working. Although the resistance to bending fatigue is generally proportional to tensile strength, if further working is applied in order to enhance the tensile strength, elongation is lowered, and the wire cannot be formed into an extra-fine copper alloy wire, such as a magnet wire. Herein, the bending strain exerted on the copper alloy wire at the time of bending fatigue increases toward the outer circumference of the wire, and the amount of bending strain decreases as the center is approached. Thus, according to the present invention, the resistance to bending fatigue can be enhanced, by work hardening the copper alloy wire by finish cold-working such that only a predetermined depth region (the wire surface section) of the wire surface has a predetermined hardness. Furthermore, while only the wire surface section is work-hardened, the entirety of the remaining portion of the wire other than the wire surface section (that is, the portion toward the deeper core than the predetermined depth, other than the wire surface section) maintains a semi-softened state. Thus, since elongation of the wire as a whole can be sufficiently secured, forming into an extra-fine copper alloy wire, such as a magnet wire, is enabled.
[0025] Among these elements, Ag is an element that can particularly enhance physical strength without lowering electrical conductivity, and is an exemplary essential additive element for the copper alloy related to the present invention used in, for example, magnet wires. In the present invention, the Ag content is set to 0.5 to 4.0 mass%, and preferably 0.5 to 2.0 mass%. If the content of Ag is too small, sufficient physical strength cannot be obtained. Also, if the Ag content is too large, electrical conductivity is lowered, and also it becomes excessively high cost.
[0026] The at least one element selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr is an another example of an essential alloying element in the copper alloy according to the present invention. In the present invention, the contents of those elements are, respectively, 0.05 to 0.3%, and preferably 0.05 % to 0.2%. If this content is too small as the respective content, the effect of strength enhancement owing to the addition of any of these elements cannot be expected in most cases. Also, if this content is too large, since the lowering of the electrical conductivity is too large, the resultant copper alloy is inappropriate as a copper alloy wire, such as a magnet wire.

[Production method]

[0027] The production method of the copper wire of the present invention will be described.
[0028] As discussed above, the shape of the copper alloy wire of the present invention is not limited to a round wire, and may also be a square wire or a rectangular wire. Then, these will be described below.

[Production method of a round wire]

[0029] First, the method of producing a copper alloy round wire of the present invention is carried out by performing the steps, for example, of: casting; intermediate cold-working; intermediate heating (intermediate annealing); final-heating (final-annealing); and finish cold-rolling, in this order. Herein, when a copper alloy wire having desired properties can be obtained without being subjected to any intermediate annealing, the intermediate annealing may be omitted.

[Casting]

[0030] To Cu, Ag and/or at least one additive element selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr is/are added, and cast in a casting machine having the interior (internal walls) preferably made of carbon, for example, in a graphite crucible. The atmosphere inside the casting machine at the time of melting is preferably selected to be a vacuum or an inert gas atmosphere, such as nitrogen or argon, in order to prevent occurrence of oxides. There are no particular limitations on the casting method, and use may be made, for example, of a transverse continuous casting machine or an upcast method. By means of such a continuous casting wire-drawing method, steps can be carried out continuously from casting to wire-drawing, and a roughly-drawn rod is cast with a diameter of generally about ϕ 8 to 23 mm.
[0031] In the case where no continuous casting wire-drawing method is utilized, a roughly-drawn rod having a diameter of generally about ϕ 8 to 23 mm is similarly obtained, by subjecting the billet (casting ingot) obtained by casting, to wire-drawing.

[Cold-working, intermediate annealing] (wire-working steps)

[0032] When this roughly-drawn rod is subjected to cold-working, the roughly-drawn rod is worked into a fine diameter wire having a diameter of ϕ 0.1 mm or less. Regarding this cold-working, it is preferable to perform cold wire-drawing.
[0033] The working ratio in this cold-working (wire-drawing) may vary depending on the target wire diameter, the copper alloy composition, and the heating or cold-working conditions thereafter, and there are no particular limitations. The working ratio is generally set to 70.0 to 99.9%.
[0034] When this cold-working includes a plurality of cold-working steps, such as first cold-working (wire-drawing) and second cold-working (wire-drawing), intermediate annealing (intermediate heating) may be carried out in the mid course of the first cold-working and the second cold-working.
[0035] The heating method of performing the intermediate annealing may be roughly classified into a batch-type method and a continuous method. Since the batch-type heating requires a longer treatment time period and a larger cost, this method is rather poor in productivity. However, since it is easy to perform the control of temperature or retention time period, it is easy to perform the control of characteristics. On the contrary, since the continuous-type heating can carry out heating and the wire-drawing continuously, this is excellent in productivity. However, since it is necessary to perform this heating in a very short time period, it is necessary to precisely control the heating temperature and time period, to realize characteristics stably. Those heating methods have advantages and disadvantages as described above, and therefore, it is desirable to select the heating method according to the purpose.
[0036] In the case of the batch-type heating, for example, it is preferable to perform heating in a heating furnace in an inert atmosphere, such as nitrogen or argon, at 300°C to 600°C for 30 minutes to 2 hours.
[0037] Examples of the continuous-type heating include an electrically heating-type heating and an in-atmosphere running-type heating. The electrically heating-type heating is a method of: providing electrode rings in the mid course of the wire-drawing step; passing an electric current to the copper alloy wire that passes among the electrode rings; and performing heating by the Joule heat generated by the copper alloy wire itself. The in-atmosphere running-type heating is a method of: providing a vessel for heating in the mid course of wire-drawing; and performing heating by passing a copper alloy wire in the atmosphere of the vessel for heating that has been heated to a predetermined temperature (for example, 300°C to 700°C). For both of those heating methods, it is preferable to perform heating in an inert gas atmosphere, in order to prevent oxidation of the copper alloy wire. In the case of the continuous-type, it is preferable to perform the heating at 300° to 700°c for 0.5 to 5 seconds.
[0038] By performing the intermediate annealing in the mod course of a plurality of cold-working steps, elongation of the wire thus obtainable can be recovered, and thereby workability can be enhanced. Also, Ag precipitation is accelerated by the intermediate annealing, and thus the physical strength and electrical conductivity of the wire thus obtainable can be further enhanced. For example, it is preferable to carry out the intermediate annealing under the conditions that satisfy the characteristics of a tensile strength of 330 MPa or more and an elongation of 10% or more of the copper alloy wire after this intermediate heating.

[Finish-annealing (also referred to as final-annealing)] (final-heating step)

[0039] The copper alloy wire that has been worked to a desired size (wire diameter) by the steps described above, is subjected to finish-annealing as the final-heating.
[0040] The heating as the finish-annealing is carried out under the conditions that satisfy the characteristics of a tensile strength of 330 MPa or more and an elongation of 10% or more of the copper alloy wire after the heating. When the finish-annealing is carried out by such a semi-softening treatment, the physical strength of the copper alloy wire itself is enhanced, the resistance to bending fatigue is enhanced, and it can be made easier to perform finish cold-working on

the surface after the heating.

[0041] Examples of the heating method of conducting finish-annealing include, similarly to the intermediate annealing, a batch-type heating and a continuous-type heating.

[0042] At the time of this finish-annealing, the tensile strength and elongation in the wire after the final-heating may undergo slight changes, depending on the composition of copper alloy wire or the working ratio. Thus, in the present invention, the heating temperature and the heating retention time period for the final heating (the finish-annealing) are appropriately adjusted such that the tensile strength of 330 MPa or more and the elongation would be 10% or more of the copper alloy wire obtainable by this finish-annealing.

[0043] In general, as the heating temperature is higher, the heating is carried out for a shorter time period, and as the heating temperature is lower, the heating is carried out for a longer time period. According to the present invention, when the finish-annealing is carried out in a batch mode, the heating is preferably carried out at 300°C to 450°C for 30 minutes to 2 hours. On the other hand, when the finish-annealing is carried out in a continuous mode, the heating is preferably carried out at 300°C to 700°C for 0.5 to 5 seconds.

[0044] When the finish-working is carried out after this final-annealing, not only the characteristics of the wire surface section of the copper alloy wire but also the characteristics of the entire copper alloy wire on the center side are slightly changed. The characteristics of the copper alloy wire before the final-annealing are adjusted, and the final-annealing conditions are determined, as described above, so that the final characteristics of the copper alloy wire obtainable by the finish cold-working after this final-annealing would give a tensile strength of 350 MPa or more and an elongation of 7% or more.

[Finish cold-working] (cold-working step)

[0045] The copper alloy wire that has been subjected to the final-heating described above is subjected to final (finish) cold-working, and thereby the copper alloy wire is hardened so as to obtain a nanoindentation hardness at the wire surface section of 1.45 GPa or more. Since the copper alloy wire of the present invention has high strength, even an extra-fine wire having a wire diameter ϕ or a wire thickness t of 0.1 mm or less can be subjected to finish cold-working. In general, the resistance to bending fatigue is proportional to tensile strength; however, when working is further applied in order to enhance the tensile strength, elongation is lowered, and the wire cannot be formed into a magnet wire or the like. The bending strain exerted on the wire at the time of bending fatigue increases toward the outer circumference of the wire, and the amount of bending strain decreases as the center is approached. Thus, the resistance to bending fatigue can be enhanced, by hardening only the wire surface section by performing finish cold-working. Furthermore, since only the wire surface section of the wire is hardened while the center side of the wire maintains a semi-softened state, elongation of the wire as a whole can be sufficiently secured, and forming into an extra-fine wire, such as a magnet wire, is also enabled. According to the present invention, the risk of wire breakage can be effectively decreased, by performing a semi-softening heating that gives characteristics of a strength of 350 MPa or more and an elongation of 7% or more in the copper alloy wire of the final product, before the wire is subjected to finish cold-working. As this finish cold-working, wire-drawing work is carried out, and the working ratio of this wire-drawing is usually 3 to 15%, preferably 5 to 15%, and more preferably 7 to 12%. If the working ratio of this finish cold-working is too low, the surface working and strength are insufficient, and the effect of enhancing the resistance to bending fatigue may be insufficient. Furthermore, if the working ratio of this finish cold-working is too high, the relevant working affects the entirety of the wire beyond the wire surface section, so that elongation is impaired, and also the risk of wire breakage in working may be increased.

[Production method of a rectangular wire]

[0046] Next, the method of producing a copper alloy rectangular wire of the present invention is the same as the method of producing a round wire described above, except for containing rectangular wire-working, and that finish cold-working appropriate for a rectangular shape is carried out. Specifically, the method of producing a rectangular wire of the present invention is carried out by performing steps of, for example, casting; intermediate cold-working (cold-wire-drawing); rectangular wire-working; final-heating (final-annealing); and finish cold-working, in this order. It is also the same as the method of producing a round wire from the viewpoint that if necessary, intermediate annealing (intermediate heating) is included between the intermediate cold-working and the rectangular wire-working. The conditions of the working/heating for the steps, such as casting, cold-working, intermediate annealing, and final-annealing, and preferred conditions thereof are also the same as those for the method of producing a round wire.

[Rectangular wire-working]

[0047] Up to the steps before the rectangular wire-working, the production work is the same as that for the round wire, in which an ingot obtained by casting is subjected to cold-working (wire-drawing) to obtain a roughly-drawn rod having a round wire shape, and the roughly-drawn rod is further subjected to intermediate annealing if necessary. Regarding the rectangular wire-working, the round wire (roughly-drawn rod) thus obtained is subjected to cold rolling using a rolling machine, cold rolling using a cassette roller die, pressing, drawing, and the like. Through this rectangular wire-working, the transverse direction (TD) cross-section shape is worked into a rectangular shape, to obtain the shape of a rectangular wire. This rolling and the like are generally carried out in one to five passes. The reduction ratio in each pass and the total reduction ratio at the time of rolling and the like are not particularly limited, and may be appropriately set to obtain a desired rectangular wire size. Herein, the reduction ratio is the ratio of change in the thickness in the rolling direction upon performing the rectangular wire-working, and when the thickness before rolling is designated as t_1, and the thickness of the wire after rolling is designated as t_2, the reduction ratio (%) is represented by: $\{1 - (t_2/t_1)\} \times 100$. For example, this total reduction ratio can be adjusted to 10 to 90%, and the reduction ratio in each pass can be adjusted to 10 to 50%. Herein, in the present invention, there are no particular limitations on the cross-section shape of the rectangular wire, but the aspect ratio is generally 1 to 50, preferably 1 to 20, and more preferably 2 to 10. The aspect ratio (represented by w/t as described below) is the ratio of a shorter side to a longer side in the rectangle that forms the transverse direction (TD) cross-section of a rectangular wire. In regard to the size of the rectangular wire, a rectangular wire thickness t is equal to the shorter side of the rectangle that forms the transverse direction (TD) cross-section, and a rectangular wire width w is equal to the longer side of the rectangle that forms the transverse direction (TD) cross-section. The rectangular wire thickness is generally 0.1 mm or less, preferably 0.08 mm or less, and more preferably 0.06 mm or less. The rectangular wire width is generally 1 mm or less, preferably 0.7 mm or less, and more preferably 0.5 mm or less.

[Finish cold-working]

[0048] Finish cold-working is carried out, in the case of a rectangular wire, in the same manner as in the rectangular wire-working. It is the same as in the case of a round wire that the rectangular wire is hardened by this finish cold-working so as to obtain a nanoindentation hardness of the wire surface section of 1.45 GPa or more. Specifically, the finish cold-working on the rectangular wire is carried out by cold rolling using a rolling machine, or cold rolling using a cassette roller die. This working ratio is usually 3 to 15%, preferably 5 to 15%, and more preferably 7 to 12%. If the working ratio of this finish cold-working is too low, surface working and strength are insufficient, and the effect of enhancing the resistance to bending fatigue may be insufficient. Furthermore, if the working ratio of this finish cold-working is too high, the relevant working affects the entirety of the wire beyond the wire surface section, elongation is impaired, and the risk of wire breakage in working may be increased.

[0049] A rectangular wire produced by such working and heating is provided with a hardened layer having a nanoindentation hardness of 1.45 GPa or more as a surface worked layer by finish cold-working, in a region extending from the wire surface toward at least 5% in depth (a region extending from the wire surface toward 20% in depth at the maximum, and preferably a region extending from the wire surface toward 15% in depth) in the upper and lower surface layers in the thickness direction. A difference lies in that in the case of the round wire, the hardened layer is retained at the surface worked layer over the entire surface of the wire in the circumferential direction, while in the case of the rectangular wire, the hardened layer is retained as the surface worked layer respectively on the upper surface and the lower surface in the thickness direction at the surface of the wire. However, the round wire and the rectangular wire (and the square wire) have a common factor that the hardened layer is retained as the surface worked layer in the wire surface section in a predetermined shallow range.

[0050] When this rectangular wire is subjected to coil working in the thickness direction, high elongation and high bending fatigue characteristics can be exhibited, similarly to the round wire according to the present invention. Herein, subjecting a rectangular wire to coil working in the thickness direction implies winding a rectangular wire into a coil shape while taking the width w of the rectangular wire as the width of the coil.

[Production method of a square wire]

[0051] Furthermore, in the case of producing a square wire, it is enough to set the transverse direction (TD) cross-section to be a square (w = t), in the method of producing a rectangular wire.

[Another embodiment of the production method of a wire]

[0052] Another embodiment of the method of producing a copper alloy wire of the present invention may be a whole production process of: first subjecting a roughly-drawn rod obtained by casting to first cold-working (wire-drawing); recovering elongation by intermediate annealing; further performing second cold-working (wire-drawing) to obtain a desired wire diameter or a desired wire thickness; and controlling a predetermined mechanical strength and elongation by final (finish) annealing; and then adjusting the nanoindentation hardness of the wire surface section by final (finish) cold-working, while simultaneously finally adjusting the entire copper alloy wire so as to have predetermined mechanical strength and elongation. However, it is preferable to reduce the number of cold-working steps, from the viewpoints of energy consumption and efficiency.

[0053] The respective working ratios for these first and second cold wire-drawings vary depending on the target wire diameter or wire thickness, the copper alloy composition, and the conditions for the two heating of intermediate annealing and finish-annealing, and there are no particular limitations on the working ratios. However, generally, the working ratio for the first cold-working (wire-drawing) is set to 70.0 to 99.9%, and the working ratio for the second cold-working (wire-drawing) is set to 70.0 to 99.9%.

[Other embodiments of the production methods of a rectangular wire and a square wire]

[0054] Instead of the production method described above, a sheet or a strip having a predetermined alloy composition is produced, and the sheet or strip is slit, to obtain a rectangular wire or square wire having a desired wire width.

[0055] This production process, for example, contains: casting, hot-rolling, cold-rolling, finish-annealing, finish cold-working, and slitting. If necessary, the intermediate annealing may be carried out in the middle of a plurality of cold rollings. Slitting may be carried out before the finish-annealing, or before the finish cold-working.

[0056] According to the production method described above, a copper alloy wire having a tensile strength of 350 MPa or more and an elongation of 7% or more is obtained.

[Wire diameter or wire thickness, usage]

[0057] There are no particular limitations on the wire diameter or the wire thickness of the copper alloy wire of the present invention. The wire diameter or the wire thickness is preferably 0.1 mm or less, more preferably 0.08 mm or less, and even more preferably 0.06 mm or less. There are no particular limitations on the lower limit of the wire diameter or the wire thickness. At the current level of technique, the lower limit is generally 0.01 mm or more.

[0058] The use of the copper alloy wire of the present invention is not particularly limited. Examples of the use include an extra-fine magnet wire, for example, of a magnet wire, for use in speaker coils that are used in mobile telephones, smart phones, and the like.

[Other physical properties]

[0059] The tensile strength of the copper alloy wire of the present invention is set to 350 MPa or more, because, if the tensile strength is less than 350 MPa, the strength is insufficient when the diameter is made finer by wire-drawing, and the wire is poor in resistance to bending fatigue.

[0060] Furthermore, the elongation of the copper alloy wire of the present invention is set to 7% or more, because, if the elongation is less than 7%, the wire is poor in workability, and the resultant wire is occurred with defects, such as wire breakage, at the time of forming into a coil.

[0061] The copper alloy wire of the present invention obtained by the above method exhibits high resistance to bending fatigue and exhibits elongation that enables forming into an extra-fine copper alloy wire, such as an extra-fine magnet wire.

EXAMPLES

[0062] The present invention will be described in more detail based on examples given below, but the invention is not meant to be limited by these.

[Examples and Comparative examples of round wires]

[0063] With respect to the cast material, the copper alloys in Examples according to this invention having the respective alloy composition, as shown in Tables 1 to 3, each containing Ag at a content of 0.5 to 4 mass%, and/or at least one selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr each at a content of 0.05 to 0.3 mass%, with the balance being Cu and unavoidable impurities; and the copper alloys in Comparative examples having the respective alloy composition as shown in Tables 1 to 3, were cast into roughly-drawn rods with diameters ϕ 10 mm, respectively, by a transverse-type continuous casting method.

[0064] Those roughly-drawn rods were subjected to cold-working (wire-drawing), intermediate annealing, finish-annealing, and finish cold-working (wire-drawing) (the total working ratio of the following first and second cold-working steps: 99.984%), to give round wire samples to have the final wire diameter of ϕ 40 μm for the Test Examples of Table 1 and Table 3, and to have the wire diameters indicated for the Test Examples of Table 2.

[0065] The heating of intermediate annealing and finish-annealing were carried out by any manner selected from three patterns of batch annealing, electric current annealing, and running annealing, each under a nitrogen atmosphere. The intermediate annealing was carried out only once in the mid course of the first cold-working (wire-drawing) and the second cold-working (wire-drawing). In the Test Examples indicated in Table 1 and Table 2, the intermediate annealing was not conducted in Test Examples. Furthermore, in the Test Examples indicated in Table 3, the intermediate annealing was conducted in some Test Examples, while not conducted in the other Test Examples. The wire diameter before the intermediate annealing after the first cold-working (wire-drawing) in the Test Examples in which intermediate annealing was carried out, is presented in the column "Wire diameter (mm)" of "Intermediate annealing" in Table 3. Regarding the working ratio of this case, the working ratio of the first cold-working (wire-drawing) was adjusted to 70.0 to 99.9%, and the working ratio of the second cold-working (wire-drawing) was adjusted to 70.0 to 99.9%.

[0066] The production conditions for the copper alloy round wires according to the present invention and the copper alloy round wire of Comparative examples, and the characteristics of the copper alloy round wires thus obtained, are presented in Tables 1 to 3.

[Examples and Comparative examples of rectangular wires]

[0067] Rectangular wire samples were produced in the same manner as the above round wires, except that rectangular wire-working was carried out after the roughly-drawn rods were subjected to cold-working (wire-drawing), or after intermediate annealing if performed, then finish-annealing was carried out, and then finish cold-working was carried out. As shown in Table 4, some samples were subjected to intermediate annealing, and the other samples were not subjected to intermediate annealing.

[0068] Regarding the rectangular wire-working, as shown in Table 4, a round wire before this working was worked by cold rolling into a rectangular wire such that the wire diameter ϕ (mm) was worked into a size of width w (mm) $\times$ thickness t (mm). The finish cold-working was carried out by cold rolling, in the same manner as in the rectangular wire-working, except that the working ratios, as indicated in Table 4.

[0069] The production conditions for the copper alloy rectangular wires according to the present invention and the copper alloy rectangular wires of Comparative examples, and the characteristics of the copper alloy rectangular wires thus obtained, are presented in Table 4.

[Characteristics/Physical properties]

[0070] With respect to the thus-obtained samples of the round wires and rectangular wires, various characteristics were tested and evaluated.

[0071] The tensile strength (TS) and elongation (El) were measured, according to JIS Z2201 and Z2241.

[0072] The number of repeating times at breakage in bending fatigue was obtained by measuring the number of repeating times until the test specimen of wire broke in a bending fatigue test, using the apparatus illustrated in Fig. 1. As illustrated in Fig. 1, a test specimen of a copper alloy wire sample with a wire diameter ϕ or wire thickness t of 0.04 mm (40 μm) was sandwiched between two dies, and a load was applied thereon by hanging a weight (W) of 10 g at the lower end of the specimen in order to suppress deflection (flexure) of the wire. In the case of the rectangular wire, the sample was mounted to be sandwiched between the two dies in the wire thickness direction (ND). The upper end of the specimen was fixed with a connecting jig. While having the specimen maintained in this state, the specimen was bended 90° on the left side and the right side, respectively, bending was repeatedly carried out at a speed of 100 times per minute, and the number of repeating times at breakage in bending was measured for each specimen, i.e. the respective sample. Regarding the number of repeating times in bending, one reciprocation of 1 $\rightarrow$ 2 $\rightarrow$ 3 in Fig. 1 was counted as one time, and the distance between the two dies was set to 1 mm so that the specimen of the copper alloy wire would not be compressed in the test. Determination of breakage was made such that the specimen was judged to be broken when the weight hung at the lower end of the specimen dropped. Furthermore, the radius of bending (R) was set to 2 mm, depending on the curvature of the dies.

[0073] The service life of a coil was evaluated as follows, based on the number of repeating times at breakage in bending fatigue measured by the test method described above. From the results of the bending fatigue test, a sample which had the number of times at breakage of 7,000 or more times was rated as "○○(excellent)", a sample which had the number of times at breakage of 5,000 times or more but less than 7,000 times was rated as "○ (good)", a sample which had the number of times at breakage of 3,000 times or more but less than 5,000 times was rated as "Δ (slightly poor)", and a sample which had the number of times at breakage of less than 3,000 times was rated as "× (poor)".

[0074] The wire-drawing property was evaluated by the presence or absence of wire breakage in wire-drawing. In this test, a test of subjecting a copper alloy wire that has been subjected to softening or semi-softening, to finish working for a length of 100 km, was performed 5 times, and a sample which could be drawn into wire without undergoing wire breakage even for once was rated as "○ (good)", a sample which underwent wire breakage once was rated as "Δ (slightly poor)", and a sample which underwent wire breakage two or more times was rated as "x (poor)".

[0075] The hardness of the wire surface section and the wire center section was measured, using a nanoindenter

(ENT-2100, manufactured by Elionix, Inc.).

[0076] The thickness (μm) of the worked layer on the surface side of the wire was determined from microstructure observation of a wire transverse cross-section (TD cross-section) and the change in hardness in the nanoindenter test, and the thickness was designated as the "surface worked layer thickness (μm)". Furthermore, from this thickness (μm) of the worked layer thus determined, the ratio (%) of the thickness from the outermost surface of the wire to the innermost core side of the worked layer, with respect to the wire diameter ϕ of wire or the wire thickness t was calculated, and the ratio was designated as the "surface worked layer thickness (%)".

[0077] Regarding the coil formability, the frequency of occurrence of wire breakage when 100 km of a copper alloy wire was subjected to coil working into a coil having a diameter of ϕ 5 mm, was tested, and a sample which did not undergo wire breakage even for once was rated as "○ (good)", a sample which underwent wire breakage once was rated as "Δ (slightly poor)", and a sample which underwent wire breakage two or more times was rated as "x (poor)".

[0078] Table 1 shows the results of measuring and evaluating the characteristics of samples of round wires of Examples (Examples 1 to 6) and samples of round wires of Comparative examples (Comparative examples 1 to 7) obtained by working and heating Cu-2% Ag alloy wires to have a final wire diameter of 0.04 mm (ϕ 40 μm). The conditions for the final-heating (finish-annealing) were changed as indicated in Table 1, and the strength and elongation before the finish cold-working were changed to various values.

Table 1

	Finish annealing			Physical properties		Working ratio at finish cold-working	Thickness of surface worked layer	Thickness of surface worked layer
	Manner	Temp.	Time	TS after heating	El after heating			
		°C		MPa	%	%	μm	%
Ex 1	Butch	390	30 min	345	18	3	2.0	5%
Ex 2	Butch	390	30 min	345	18	5	2.8	7%
Ex 3	Butch	390	30 min	345	18	7	3.6	9%
Ex 4	Butch	400	30 min	335	21	10	4.0	10%
Ex 5	Butch	400	30 min	335	21	12	6.0	15%
Ex 6	Butch	410	30 min	330	25	15	8.0	20%
C ex 1	Butch	410	30 min	330	25	0	0.0	0%
C ex 2	Butch	400	30 min	335	20	1	0.4	1%
C ex 3	Butch	390	30 min	345	20	2	1.2	3%
C ex 4	Butch	400	30 min	335	23	17	11.2	28%
C ex 5	Butch	390	30 min	345	23	20	16.0	40%
C ex 6	Butch	250	30 min	410	6	10	4.0	10%
C ex 7	Butch	500	30 min	305	35	10	3.6	9%

Cu-2%Ag

Final wire-diameter: φ0.04mm

"Ex" means Example; and "C ex" means Comparative example. The same is applied to hereinafter.

Table 1 (cont.)

	Physical properties							
	Hardness at wire surface portion	Hardness at wire central portion	TS after finish cold-working	El after finish cold-working	The number of repeating times at breakage in bending	Coil life	Breakage in wire-drawing	Coil formability
	GPa	GPa	MPa	%	times			
Ex 1	1.46	1.29	361	17	6,534	○	○	○
Ex 2	1.51	1.24	357	14	6,835	○	○	○
Ex 3	1.63	1.23	363	13	8,740	○○	○	○
Ex 4	1.53	1.29	367	11	9,476	○○	○	○
Ex 5	1.64	1.27	378	13	7,839	○○	○	○
Ex 6	1.46	1.30	391	8	6,626	○	○	○
C ex 1	1.25	1.25	330	25	2,878	×	×	○
C ex 2	1.43	1.20	351	18	2,901	×	○	○
C ex 3	1.52	1.20	350	14	3,060	□	○	○
C ex 4	1.53	1.32	415	3	6,819	○	□	×
C ex 5	1.64	1.35	426	4	8,123	○○	□	×
C ex 6	1.85	1.80	425	4	7,824	○○	○	×
C ex 7	1.37	1.10	328	19	2,268	×	×	○

[0079] As shown in Examples 1 to 6, it is understood that when a copper alloy wire that had been subjected to a final-heating (finish-annealing) so as to have a tensile strength of 330 MPa or more and an elongation of 10% or more, was subjected to finish cold-working at a working ratio of 3 to 15%, a worked layer having a nanoindentation hardness of 1.45 GPa or more was formed in the wire surface section, and the resistance to bending fatigue could be enhanced. Furthermore, as shown in Examples 3 to 5, when the working ratio of the finish cold-working was 7 to 12%, the effect of enhancing the resistance to bending fatigue is superior, and thus it is preferable.

[0080] On the contrary, in a case in which the finish cold-working for providing this wire surface section was not carried out as in Comparative example 1, or in a case in which the working ratio for the finish cold-working was too small such as less than 3% as in Comparative example 2 or 3, no worked layer did exist at all, or the layer thickness of the worked layer was so thin that the resistance to bending fatigue could not be enhanced. Furthermore, in a case in which the working ratio of the finish cold-working was too large such as more than 15% as in Comparative example 4 or 5, working proceeded not only on the wire surface section, but also to the entire copper alloy wire including the center side. Thus, the surface worked layer that enhances the resistance to bending fatigue was not satisfactorily formed, the copper alloy wires after the finish cold-working were poor in elongation, and the resistance to bending fatigue could not be enhanced.

[0081] Furthermore, in a case in which the final-heating before the finish cold-working is insufficient, and the elongation is less than 10% as in Comparative example 6, the elongation of the copper alloy wire after finish cold-working is less than 7%, and insufficient coil formability is obtained. Furthermore, if softening is carried out excessively as the final-heating before the finish cold-working as illustrated in Comparative example 7, and the tensile strength of the copper alloy wire is less than 330 MPa, the hardness of the wire surface section is insufficient, and the strength after the finish-annealing is also insufficient. Furthermore, wire breakage at the time of finish cold-working is brought about.

[0082] Meanwhile, also in the case of rectangular wires, the same results as in the case of the round wires can be obtained.

[0083] In Examples 7 to 12 and Comparative examples 8 and 9, the results for evaluating the wire-drawing property when Cu-1% Ag alloy round wires having various diameters obtained by changing the conditions for the final-heating (finish-annealing) as indicated in Table 2, and varying the strength before the finish cold-working to various values, were subjected to finish cold-working at a working ratio of 10%. In Comparative examples 10 and 11, the test was carried out in the same manner as described above, except that Cu-0.3% Ag alloy round wires were used instead of the Cu-1% Ag alloy wires.

[0084] For the wire-drawing property, a test of subjecting a copper alloy wire that has been subjected to softening or semi-softening, to finish working for a length of 100 km, was performed 5 times, and a sample which could be drawn into wire without undergoing wire breakage even for once was rated as "○ (good)", a sample which underwent wire breakage once was rated as "Δ (slightly poor)", and a sample which underwent wire breakage two or more times was rated as "× (poor)".

[0085] It is understood that in the case of performing wire-drawing on a relatively thick wire with wire diameter ϕ 0.5 mm or more, wire-drawing can be achieved without any wire breakage; however, in the case of subjecting a wire with diameter ϕ 0.1 mm or less to wire-drawing, the tensile strength of the copper alloy wire after the finish-annealing before the wire-drawing working is preferably 330 MPa or more. Thus, it is understood that the resistance to bending fatigue can be enhanced, by performing surface working on a fine wire having a diameter of ϕ 0.1 mm or less, under the production conditions defined in the production method of the present invention.

[0086] Meanwhile, also in the case of rectangular wires, the same results as in the case of the round wires can be obtained.

Table 2

	Finish annealing			TS after finish heating	Wire-drawability (whether or not breakage in wire-drawing)						
	Manner	Temp.	Time		Wire diameter (mm)						
		°C		MPa	0.02	0.04	0.06	0.08	0.1	0.5	1
Ex 7	Butch	420	30 min	333	□	□	○	○	○	○	○
Ex 8	Butch	410	30 min	342	□	○	○	○	○	○	○
Ex 9	Butch	400	30 min	353	○	○	○	○	○	○	○
Ex 10	Butch	390	30 min	367	○	○	○	○	○	○	○
Ex 11	Butch	380	30 min	382	○	○	○	○	○	○	○
Ex 12	Butch	370	30 min	398	○	○	○	○	○	○	○
C ex 8	Butch	440	30 min	305	×	×	×	×	□	○	○
C ex 9	Butch	430	30 min	325	×	×	×	×	□	○	○
C ex 10	Butch	360	30 min	305	×	×	×	×	□	○	○

(continued)

	Finish annealing			TS after finish heating	Wire-drawability (whether or not breakage in wire-drawing)						
	Manner	Temp.	Time		Wire diameter (mm)						
		°C		MPa	0.02	0.04	0.06	0.08	0.1	0.5	1
C ex 11	Butch	350	30 min	325	×	×	×	×	□	○	○
Note: Ex 7 to 12 and C ex 8 to 9: Cu-1%Ag C ex 10 to 11: Cu-0.3%Ag The range enclosed with double-line indicates the working examples according to this invention.											

[0087] Table 3 shows Examples according to the present invention and Comparative examples of round wires produced from copper alloys of various other alloy compositions. It is understood that when copper alloy wires having a tensile strength of 330 MPa or more and an elongation of 10% or more are produced by a final-heating (finish-annealing) before the finish cold-working, finish cold-working can be performed to obtain a diameter of ϕ 0.1 mm or less, at a working ratio of 3 to 15%, preferably 5 to 15%, and more preferably 7 to 12%.

[0088] Furthermore, it was found that when wires are subjected to predetermined surface working by this finish cold-working at a working ratio of 3 to 15%, preferably 5 to 15%, and more preferably 7 to 12%, the resistance to bending fatigue of the copper alloy wires can be enhanced, and a magnet wire having sufficient coil formability with an elongation after finish cold-working of 7% or more, and preferably 10% or more, and having a long coil service life can be obtained.

[0089] Particularly, from a comparison between Comparative examples and Examples according to the present invention, it is understood that when the nanoindentation hardness in a depth region extending from the outermost surface of the wire toward at least 5% inner side in the wire diameter is 1.45 GPa or more, and the final wire has a tensile strength of 350 MPa or more and an elongation of 7% or more, desired physical properties can be achieved.

Table 3

	Composition*								
	Ag	Mg	Sn	In	Zn	Ni	Cr	Zr	Co
	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%
Ex 13	0.5	-	-	-	-	-	-	-	-
Ex 14	0.5	-	-	-	-	-	-	-	-
Ex 15	0.5	-	-	-	-	-	-	-	-
Ex 16	0.5	-	-	-	-	-	-	-	-
Ex 17	1	-	-	-	-	-	-	-	-
Ex 18	1	-	-	-	-	-	-	-	-
Ex 19	1	-	-	-	-	-	-	-	-
Ex 20	1	-	-	-	-	-	-	-	-
Ex 21	3	-	-	-	-	-	-	-	-
Ex 22	3	-	-	-	-	-	-	-	-
Ex 23	3	-	-	-	-	-	-	-	-
Ex 24	3	-	-	-	-	-	-	-	-
Ex 25	4	-	-	-	-	-	-	-	-
Ex 26	4	-	-	-	-	-	-	-	-
Ex 27	4	-	-	-	-	-	-	-	-
Ex 28	4	-	-	-	-	-	-	-	-
Ex 29	-	0.1	-	-	-	-	-	-	-
Ex 30	-	0.1	-	-	-	-	-	-	-
Ex 31	-	0.1	-	-	-	-	-	-	-
Ex 32	-	0.1	-	-	-	-	-	-	-
Ex 33	-	0.3	-	-	-	-	-	-	-
Ex 34	-	0.3	-	-	-	-	-	-	-
Ex 35	-	0.3	-	-	-	-	-	-	-
Ex 36	-	0.3	-	-	-	-	-	-	-

Final wire-diameter: φ0.04mm

Note: * The balance was Cu and inevitable impurities. "-" means not added.

Table 3 (cont.-1)

	Intermediate annealing				Finish annealing			Physical properties	
	Wire diameter	Manner	Temp.	Time	Manner	Temp.	Time	TS after finish annealing	El after finish annealing
	mm		°C			°C		MPa	%
Ex 13	None				Butch	370	1 hr	340	18
Ex 14	None				Running	500	1 sec	335	16
Ex 15	None				Butch	370	30 min	338	15
Ex 16	0.5	Butch	400	1 hr	Butch	370	1 hr	339	16
Ex 17	None				Electric	550	1 sec	335	19
Ex 18	None				Butch	380	1 hr	333	20
Ex 19	None				Running	550	2 sec	332	20
Ex 20	1	Running	500	1 sec	Running	550	1 sec	340	18
Ex 21	None				Running	610	0.5 sec	347	22
Ex 22	None				Butch	420	30 min	343	19
Ex 23	None				Butch	420	2 hr	345	20
Ex 24	0.5	Electric	500	1 sec	Running	610	1 sec	349	18
Ex 25	None				Running	650	1 sec	361	20
Ex 26	None				Running	700	0.5 sec	356	16
Ex 27	None				Butch	450	1 hr	354	19
Ex 28	0.4	Running	650	1 sec	Running	700	1 sec	350	17
Ex 29	None				Running	400	1 sec	351	19
Ex 30	None				Running	400	2 sec	346	18
Ex 31	None				Butch	330	30 min	342	19
Ex 32	0.4	Butch	600	2 hr	Butch	300	1 hr	339	22
Ex 33	None				Electric	400	0.5 sec	342	26
Ex 34	None				Running	420	1 sec	345	24
Ex 35	None				Butch	300	2 hr	348	20
Ex 36	0.3	Running	600	1 sec	Running	400	1 sec	341	24

Table 3 (cont.-2)

	Working ratio at finish cold-working	Thickness of surface worked layer	Thickness of surface worked layer	Physical properties							
				Hardness at wire surface portion	Hardness at wire central portion	TS after finish cold-working	El after finish cold-working	The number of repeating times at breakage in bending	Coil life	Breakage in wire-drawing	Coil formability
	%	μm	%	GPa	GPa	MPa	%	times			
Ex 13	3	2.0	5%	1.46	1.29	356	15	6,167	○	○	○
Ex 14	10	4.0	10%	1.47	1.25	357	13	9,126	○○	○	○
Ex 15	12	5.6	14%	1.50	1.20	373	8	7,504	○○	○	○
Ex 16	10	4.0	10%	1.49	1.22	361	13	8,123	○○	○	○
Ex 17	7	3.2	8%	1.46	1.23	357	14	8,433	○○	○	○
Ex 18	10	4.0	10%	1.47	1.30	358	13	7,784	○○	○	○
Ex 19	12	5.6	14%	1.60	1.30	361	8	7,935	○○	○	○
Ex 20	7	3.2	8%	1.56	1.28	362	13	7,900	○○	○	○
Ex 21	5	2.4	6%	1.45	1.25	384	15	6,707	○	○	○
Ex 22	7	3.2	8%	1.61	1.20	368	13	9,080	○○	○	○
Ex 23	10	4.0	10%	1.69	1.23	365	12	9,770	○○	○	○
Ex 24	7	3.2	8%	1.52	1.27	370	13	8,923	○○	○	○
Ex 25	5	2.4	6%	1.50	1.20	376	17	5,938	○	○	○
Ex 26	10	4.0	10%	1.49	1.22	375	10	8,298	○○	○	○
Ex 27	12	5.6	14%	1.46	1.21	389	8	8,766	○○	○	○
Ex 28	10	4.0	10%	1.59	1.25	380	10	8,901	○○	○	○
Ex 29	5	2.4	6%	1.45	1.26	367	14	6,197	○	○	○
Ex 30	7	3.2	8%	1.50	1.25	356	14	7,071	○○	○	○
Ex 31	15	8.0	20%	1.62	1.20	356	8	6,918	○	○	○
Ex 32	7	3.2	8%	1.47	1.29	355	19	7,212	○○	○	○
Ex 33	3	2.0	5%	1.47	1.30	357	20	5,591	○	○	○
Ex 34	7	3.2	8%	1.73	1.27	352	22	8,792	○○	○	○
Ex 35	12	5.6	14%	1.45	1.21	364	8	7,441	○○	○	○
Ex 36	12	6.4	16%	1.47	1.23	359	9	7,025	○○	○	○

Table 3 (cont.-3)

	Composition								
	Ag	Mg	Sn	In	Zn	Ni	Cr	Zr	Co
	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%
Ex 37	-	-	0.1	-	-	-	-	-	-
Ex 38	-	-	0.3	-	-	-	-	-	-
Ex 39	-	-	-	0.1	-	-	-	-	-
Ex 40	-	-	-	0.3	-	-	-	-	-
Ex 41	-	-	-	-	0.1	-	-	-	-
Ex 42	-	-	-	-	0.3	-	-	-	-
Ex 43	-	-	-	-	-	0.1	-	-	-
Ex 44	-	-	-	-	-	0.3	-	-	-
Ex 45	-	-	-	-	-	-	0.1	-	-
Ex 46	-	-	-	-	-	-	0.3	-	-
Ex 47	-	-	-	-	-	-	-	0.1	-
Ex 48	-	-	-	-	-	-	-	0.3	-
Ex 49	-	-	-	-	-	-	-	-	0.1
Ex 50	-	-	-	-	-	-	-	-	0.3
Ex 51	0.5	0.1	-	-	-	-	-	-	-
Ex 52	0.5	0.1	-	-	-	-	-	-	-
Ex 53	0.5	0.2	-	-	-	-	-	-	-
Ex 54	0.5	0.2	-	-	-	-	-	-	-
Ex 55	1	0.05	-	-	-	-	-	-	-
Ex 56	1	0.1	-	-	-	-	-	-	-
Ex 57	1	0.1	-	-	-	-	-	-	-
Ex 58	2	-	0.05	-	-	-	-	-	-
Ex 59	-	0.15	-	-	0.2	-	-	-	-
Ex 60	-	0.1	-	0.1	-	-	-	-	-
Ex 61	1	-	-	0.1	-	-	-	-	-
Ex 62	1	-	-	-	-	-	-	0.1	-
Ex 63	1	0.05	-	-	-	-	-	0.1	-
Ex 64	-	0.1	-	-	-	-	-	0.1	-

Final wire-diameter: φ0.04mm

Table 3 (cont.-4)

	Intermediate annealing				Finish annealing			Physical properties	
	Wire diameter	Manner	Temp.	Time	Manner	Temp.	Time	TS after finish annealing	El after finish annealing
	mm		°C			°C		MPa	%
Ex 37	None				Electric	400	3 sec	349	26
Ex 38	None				Running	420	1 sec	338	23
Ex 39	None				Butch	300	1 hr	349	24
Ex 40	None				Butch	300	1 hr	351	22
Ex 41	None				Running	400	0.5 sec	338	23
Ex 42	None				Electric	380	5 sec	346	25
Ex 43	None				Butch	300	2 hr	343	20
Ex 44	None				Butch	300	1 hr	341	17
Ex 45	None				Running	400	1 sec	351	15
Ex 46	None				Running	380	2 sec	352	14
Ex 47	None				Butch	300	30 min	361	18
Ex 48	None				Running	400	4 sec	356	21
Ex 49	None				Electric	400	0.5 sec	341	21
Ex 50	None				Running	400	1 sec	342	19
Ex 51	None				Running	500	2 sec	351	20
Ex 52	None				Electric	500	0.5 sec	348	15
Ex 53	None				Butch	400	1 hr	352	21
Ex 54	0.5	Butch	450	30 min	Electric	500	1 sec	350	22
Ex 55	None				Butch	380	2 hr	338	22
Ex 56	None				Running	550	1 sec	352	21
Ex 57	0.5	Running	600	1 sec	Butch	400	30 min	345	19
Ex 58	None				Running	580	1 sec	336	23
Ex 59	None				Butch	300	30 min	333	19
Ex 60	None				Running	300	1 sec	342	21
Ex 61	None				Electric	550	0.5 sec	346	23
Ex 62	None				Running	550	2 sec	351	23
Ex 63	None				Electric	550	2 sec	365	19
Ex 64	None				Butch	300	1 hr	349	21

Table 3 (cont.-5)

	Working ratio at finish cold-working	Thickness of surface worked layer	Thickness of surface worked layer	Physical properties							
				Hardness at wire surface portion	Hardness at wire central portion	TS after finish cold-working	El after finish cold-working	The number of repeating times at breakage in bending	Coil life	Breakage in wire-drawing	Coil formability
	%	μm	%	GPa	GPa	MPa	%	times			
Ex 37	7	3.2	8%	1.48	1.26	359	19	9,067	○○	○	○
Ex 38	10	4.0	10%	1.50	1.28	354	12	9,139	○○	○	○
Ex 39	3	2.0	5%	1.52	1.29	358	20	5,720	○	○	○
Ex 40	10	4.0	10%	1.64	1.25	360	10	8,984	○○	○	○
Ex 41	7	3.2	8%	1.49	1.27	356	17	8,020	○○	○	○
Ex 42	10	4.0	10%	1.48	1.26	358	11	7,726	○○	○	○
Ex 43	10	4.0	10%	1.62	1.20	356	11	7,423	○○	○	○
Ex 44	12	4.8	12%	1.53	1.29	360	8	9,069	○○	○	○
Ex 45	5	2.8	7%	1.46	1.24	367	10	5,697	○	○	○
Ex 46	7	3.2	8%	1.45	1.23	367	13	7,951	○○	○	○
Ex 47	12	5.6	14%	1.47	1.25	379	8	7,754	○○	○	○
Ex 48	7	3.2	8%	1.50	1.27	375	11	7,211	○○	○	○
Ex 49	10	4.0	10%	1.77	1.29	368	12	8,478	○○	○	○
Ex 50	13	7.2	18%	1.50	1.28	359	9	8,261	○○	○	○
Ex 51	10	4.0	10%	1.52	1.29	358	10	9,002	○○	○	○
Ex 52	12	5.6	14%	1.52	1.29	360	8	8,118	○○	○	○
Ex 53	10	4.0	10%	1.47	1.25	365	10	7,418	○○	○	○
Ex 54	12	5.6	14%	1.56	1.29	371	7	7,259	○○	○	○
Ex 55	7	2.8	7%	1.46	1.28	355	15	7,716	○○	○	○
Ex 56	10	4.0	10%	1.54	1.30	378	13	8,056	○○	○	○
Ex 57	7	3.2	8%	1.54	1.29	369	16	7,894	○○	○	○
Ex 58	7	3.2	8%	1.55	1.27	357	14	9,957	○○	○	○
Ex 59	10	4.0	10%	1.63	1.25	357	12	9,824	○○	○	○
Ex 60	12	5.6	14%	1.51	1.20	357	9	8,425	○○	○	○
Ex 61	7	3.2	8%	1.52	1.29	358	19	9,951	○○	○	○
Ex 62	10	4.0	10%	1.70	1.30	371	16	9,100	○○	○	○
Ex 63	10	4.0	10%	1.45	1.31	381	10	8,916	○○	○	○
Ex 64	10	4.0	10%	1.50	1.28	368	16	9,017	○○	○	○

Table 3 (cont.-6)

	Composition*								
	Ag	Mg	Sn	In	Zn	Ni	Cr	Zr	Co
	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%
C ex 12	0.5	-	-	-	-	-	-	-	-
C ex 13	1	-	-	-	-	-	-	-	-
C ex 14	1	-	-	-	-	-	-	-	-
C ex 15	1	-	-	-	-	-	-	-	-
C ex 16	3	-	-	-	-	-	-	-	-
C ex 17	3	-	-	-	-	-	-	-	-
C ex 18	3	-	-	-	-	-	-	-	-
C ex 19	-	0.1	-	-	-	-	-	-	-
C ex 20	-	0.1	-	-	-	-	-	-	-
C ex 21	-	0.3	-	-	-	-	-	-	-
C ex 22	-	0.3	-	-	-	-	-	-	-
C ex 23	-	-	0.2	-	-	-	-	-	-
C ex 24	-	-	0.2	-	-	-	-	-	-
C ex 25	-	-	-	0.1	-	-	-	-	-
C ex 26	-	-	-	0.1	-	-	-	-	-
C ex 27	-	-	-	-	0.1	-	-	-	-
C ex 28	-	-	-	-	0.1	-	-	-	-
C ex 29	-	-	-	-	-	0.1	-	-	-
C ex 30	-	-	-	-	-	0.1	-	-	-
C ex 31	0.1	-	-	-	-	-	-	-	-
C ex 32	-	-	0.05	-	-	-	-	-	-
C ex 33	-	-	-	-	-	-	-	-	-
C ex 34	0.5	-	-	-	-	-	-	-	-
C ex 35	1	-	-	-	-	-	-	-	-
C ex 36	1	-	-	-	-	-	-	-	-
C ex 37	-	0.2	-	-	-	-	-	-	-
C ex 38	-	-	0.2	-	-	-	-	-	-
C ex 39	-	-	0.2	-	-	-	-	-	-
C ex 40	-	-	-	0.1	-	-	-	-	-
C ex 41	-	-	-	-	0.2	-	-	-	-
C ex 42	-	-	-	-	-	0.2	-	-	-

Final wire-diameter: φ0.04mm

Table 3 (cont.-7)

	Intermediate annealing				Finish annealing			Physical properties	
	Wire diameter	Manner	Temp.	Time	Manner	Temp.	Time	TS after finish annealing	El after finish annealing
	mm		°C			°C		MPa	%
C ex 12	None				Running	500	0.5 sec	335	20
C ex 13	None				Running	550	1 sec	335	20
C ex 14	None				Butch	380	1 hr	341	20
C ex 15	0.2	Running	500	1 sec	Running	550	1 sec	340	21
C ex 16	None				Running	610	1 sec	337	24
C ex 17	None				Electric	610	2 sec	341	16
C ex 18	0.3	Butch	550	1 hr	Butch	420	1 hr	345	18
C ex 19	None				Running	400	1 sec	355	19
C ex 20	None				Butch	300	1 hr	352	19
C ex 21	None				Butch	300	30 min	348	18
C ex 22	None				Electric	400	1 sec	351	26
C ex 23	None				Butch	280	2 hr	344	21
C ex 24	None				Running	400	3 sec	346	23
C ex 25	None				Running	400	1 sec	349	23
C ex 26	None				Running	400	1 sec	351	27
C ex 27	None				Butch	290	2 hr	345	20
C ex 28	None				Butch	300	1 hr	344	29
C ex 29	None				Running	380	1 sec	347	23
C ex 30	None				Butch	300	30 min	345	22
C ex 31	None				Electric	450	2 sec	301	25
C ex 32	None				Butch	400	1 hr	289	27
C ex 33	None				Running	350	1 sec	251	26
C ex 34	None				Butch	500	1 hr	286	39
C ex 35	None				Running	600	0.5 sec	287	37
C ex 36	0.2	Butch	500	1 hr	Butch	600	1 hr	271	37
C ex 37	None				Electric	450	2 sec	291	38
C ex 38	None				Butch	400	30 min	289	37
C ex 39	0.4	Running	500	1 sec	Running	500	1 sec	261	39
C ex 40	None				Running	450	3 sec	300	39
C ex 41	None				Running	500	0.5 sec	276	38
C ex 42	None				Butch	400	1 hr	268	39

Table 3 (cont.-8)

	Working ratio at finish cold-working	Thickness of surface worked layer	Thickness of surface worked layer	Physical properties							
				Hardness at wire surface portion	Hardness at wire central portion	TS after finish cold-working	El after finish cold-working	The number of repeating times at breakage in bending	Coil life	Breakage in wire-drawing	Coil formability
	%	μm	%	GPa	GPa	MPa	%	times			
C ex 12	20	16.0	40%	1.46	1.30	406	6	6,891	○	□	×
C ex 13	1	0.8	2%	1.50	1.33	340	18	2,924	×	○	○
C ex 14	30	20.0	50%	1.50	1.35	406	6	7,514	○○	□	×
C ex 15	20	12.8	32%	1.47	1.31	371	6	6,421	○	□	×
C ex 16	2	0.8	2%	1.44	1.29	364	19	2,516	×	○	○
C ex 17	20	17.6	44%	1.52	1.37	389	3	7,236	○○	×	×
C ex 18	2	0.8	2%	1.44	1.32	365	14	3,845	□	○	○
C ex 19	2	0.8	2%	1.44	1.29	365	15	3,114	□	○	○
C ex 20	20	16.8	42%	1.53	1.39	400	5	7,532	○○	×	×
C ex 21	1	0.8	2%	1.41	1.30	358	16	3,109	□	○	○
C ex 22	22	14.4	36%	1.55	1.45	394	3	7,128	○○	×	×
C ex 23	1	0.8	2%	1.42	1.30	359	14	3,927	□	○	○
C ex 24	20	12.0	30%	1.43	1.30	392	4	6,101	○	×	×
C ex 25	2	0.8	2%	1.40	1.29	356	19	3,470	□	○	○
C ex 26	25	10.4	26%	1.42	1.30	401	2	8,124	○○	□	×
C ex 27	2	0.8	2%	1.41	1.25	359	16	3,764	□	○	○
C ex 28	20	12.8	32%	1.40	1.27	396	4	6,541	○	□	×
C ex 29	2	0.8	2%	1.41	1.26	357	19	3,216	□	○	○
C ex 30	20	12.0	30%	1.44	1.30	405	3	7,141	○○	□	×
C ex 31	10	4.0	10%	1.23	1.10	320	18	2,821	×	×	○
C ex 32	10	4.0	10%	1.15	1.05	305	18	2,764	×	×	○
C ex 33	10	4.0	10%	1.01	0.93	278	19	2,056	×	×	○
C ex 34	10	4.0	10%	1.16	1.05	308	33	2,835	×	×	○
C ex 35	10	4.0	10%	1.06	0.96	309	33	2,501	×	×	○
C ex 36	10	4.0	10%	1.18	1.07	312	30	2,308	×	×	○
C ex 37	10	4.0	10%	1.15	1.05	310	32	2,996	×	×	○
C ex 38	10	4.0	10%	1.17	1.10	302	31	2,963	×	×	○
C ex 39	10	4.0	10%	1.11	1.01	298	34	2,812	×	×	○
C ex 40	10	4.0	10%	1.18	1.05	312	32	2,845	×	×	○
C ex 41	10	4.0	10%	1.05	0.94	290	32	2,720	×	×	○
C ex 42	10	4.0	10%	1.16	1.05	280	34	2,973	×	×	○

[0090] Table 4 shows Examples according to the present invention and Comparative examples of rectangular wires produced from copper alloys of various alloy compositions. From the results shown in Table 4, also in the case of rectangular wires, the same results as in the case of the round wires can be obtained.

Table 4

	Composition*								
	Ag	Mg	Sn	In	Zn	Ni	Cr	Zr	Co
	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%
Ex 65	0.5	-	-	-	-	-	-	-	-
Ex 66	1	-	-	-	-	-	-	-	-
Ex 67	3	-	-	-	-	-	-	-	-
Ex 68	4	-	-	-	-	-	-	-	-
Ex 69	-	0.1	-	-	-	-	-	-	-
Ex 70	-	-	0.3	-	-	-	-	-	-
Ex 71	-	-	-	0.3	-	-	-	-	-
Ex 72	-	-	-	-	-	0.3	-	-	-
Ex 73	-	-	-	-	-	-	0.1	-	-
Ex 74	-	-	-	-	-	-	-	-	0.3
Ex 75	1	0.1	-	-	-	-	-	-	-
Ex 76	1	0.1	-	-	-	-	-	-	-
Ex 77	2	-	0.05	-	-	-	-	-	-
Ex 78	-	0.15	-	-	0.2	-	-	-	-
Ex 79	1	-	-	-	-	-	-	0.1	-
Ex 80	1	0.05	-	-	-	-	-	0.1	-

Note: * The balance was Cu and inevitable impurities. "-" means not added.

Table 4 (cont.-1)

	Intermediate annealing				Rectangular wire-working
	Wire diameter	Manner	Temp.	Time	Wire diameter Φ (mm) before working→ width w (mm) × thickness t (mm) after working
	mm		°C		
Ex 65	None				Φ0.1→0.2×0.025
Ex 66	1	Running	500	1 sec	Φ0.12→0.15×0.05
Ex 67	None				Φ0.1→0.3×0.015
Ex 68	0.4	Running	650	1 sec	Φ0.15→0.2×0.08
Ex 69	None				Φ0.15→0.28×0.045
Ex 70	None				Φ0.1→0.3×0.015
Ex 71	None				Φ0.12→0.1×0.08
Ex 72	None				Φ0.08→0.15×0.03
Ex 73	None				Φ0.2→0.45×0.06
Ex 74	None				Φ0.12→0.45×0.02
Ex 75	None				Φ0.15→0.17×0.1
Ex 76	0.5	Running	600	1 sec	Φ0.1→0.3×0.015
Ex 77	None				Φ0.15→0.1×0.05
Ex 78	None				Φ0.1→0.3×0.015
Ex 79	None				Φ0.15→0.28×0.035
Ex 80	None				Φ0.08→0.15×0.03

Table 4 (cont.-2)

	Finish annealing			Physical properties		Working ratio at finish cold-working	Thickness of surface worked layer	Thickness of surface worked layer
	Manner	Temp.	Time	TS after finish-annealing	El after finish-annealing			
		°C		MPa	%	%	µm	%
Ex 65	Butch	370	1 hr	340	18	3	1.3	5%
Ex 66	Running	550	1 sec	340	18	7	3.5	7%
Ex 67	Running	610	0.5 sec	347	22	5	1.2	8%
Ex 68	Running	700	1 sec	350	17	10	8.8	11%
Ex 69	Running	400	1 sec	351	19	5	3.2	7%
Ex 70	Running	420	1 sec	338	23	10	1.7	11%
Ex 71	Butch	300	1 hr	351	22	10	8.0	10%
Ex 72	Butch	300	1 hr	341	17	12	3.6	12%
Ex 73	Running	400	1 sec	351	15	5	4.2	7%
Ex 74	Running	400	1 sec	342	19	13	3.6	18%
Ex 75	Running	550	1 sec	352	21	10	10.0	10%
Ex 76	Butch	400	30 min	345	19	7	1.2	8%
Ex 77	Running	580	1 sec	336	23	7	4.0	8%
Ex 78	Butch	300	30 min	333	19	10	1.5	10%
Ex 79	Running	550	2 sec	351	23	10	3.5	10%
Ex 80	Electric	550	2 sec	365	19	10	3.0	10%

Table 4 (cont.-3)

	Physical properties							
	Hardness at wire surface portion	Hardness at wire central portion	TS after finish cold-working	El after finish cold-working	The number of repeating times at breakage in bending	Coil life	Breakage in wire-drawing	Coil formability
	GPa	GPa	MPa	%	times			
Ex 65	1.47	1.30	362	14	6,545	○	○	○
Ex 66	1.56	1.28	363	15	7,684	○○	○	○
Ex 67	1.45	1.25	382	13	6,521	○	○	○
Ex 68	1.59	1.25	380	11	8,218	○○	○	○
Ex 69	1.45	1.26	365	13	6,534	○	○	○
Ex 70	1.51	1.27	352	12	8,945	○○	○	○
Ex 71	1.62	1.25	362	11	8,678	○○	○	○
Ex 72	1.52	1.28	358	9	9,154	○○	○	○
Ex 73	1.48	1.24	365	10	5,789	○	○	○
Ex 74	1.51	1.27	357	9	8,315	○○	○	○
Ex 75	1.53	1.30	377	12	8,145	○○	○	○
Ex 76	1.55	1.28	369	17	7,648	○○	○	○
Ex 77	1.53	1.25	356	13	9,874	○○	○	○
Ex 78	1.65	1.27	357	12	9,798	○○	○	○
Ex 79	1.68	1.30	371	16	9,345	○○	○	○
Ex 80	1.47	1.29	380	11	8,649	○○	○	○

Table 4 (cont.-4)

	Composition								
	Ag	Mg	Sn	In	Zn	Ni	Cr	Zr	Co
	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%
C ex 43	0.5	-	-	-	-	-	-	-	-
C ex 44	1	-	-	-	-	-	-	-	-
C ex 45	3	-	-	-	-	-	-	-	-
C ex 46	3	-	-	-	-	-	-	-	-
C ex 47	-	0.1	-	-	-	-	-	-	-
C ex 48	-	0.1	-	-	-	-	-	-	-
C ex 49	-	0.3	-	-	-	-	-	-	-
C ex 50	-	-	-	0.1	-	-	-	-	-
C ex 51	-	-	-	-	0.1	-	-	-	-
C ex 52	-	-	-	-	-	0.1	-	-	-
C ex 53	0.1	-	-	-	-	-	-	-	-
C ex 54	-	-	0.05	-	-	-	-	-	-
C ex 55	-	-	-	-	-	-	-	-	-
C ex 56	0.5	-	-	-	-	-	-	-	-
C ex 57	1	-	-	-	-	-	-	-	-

Table 4 (cont.-5)

	Intermediate annealing				Rectangular wire-working
	Wire diameter	Manner	Temp.	Time	Wire diameter Φ (mm) before working→ width w (mm) × thickness t (mm) after working
	mm		°C		
C ex 43	None				Φ0.1→0.2×0.025
C ex 44	None				Φ0.12→0.15×0.05
C ex 45	None				Φ0.15→0.2×0.08
C ex 46	0.3	Butch	550	1 hr	Φ0.15→0.1×0.05
C ex 47	None				Φ0.1→0.3×0.015
C ex 48	None				Φ0.2→0.45×0.06
C ex 49	None				Φ0.12→0.45×0.02
C ex 50	None				Φ0.15→0.17×0.1
C ex 51	None				Φ0.1→0.3×0.015
C ex 52	None				Φ0.15→0.1×0.05
C ex 53	None				Φ0.08→0.15×0.03
C ex 54	None				Φ0.15→0.17×0.1
C ex 55	None				Φ0.15→0.2×0.08
C ex 56	None				Φ0.15→0.1×0.05
C ex 57	0.2	Butch	500	1 hr	Φ0.2→0.45×0.06

Table 4 (cont.-6)

	Finish annealing			Physical properties		Working ratio at finish cold-working	Thickness of surface worked layer	Thickness of surface worked layer
	Manner	Temp.	Time	TS after finish-annealing	El after finish-annealing			
		°C		MPa	%	%	µm	%
C ex 43	Running	500	0.5 sec	335	20	20	10.0	40%
C ex 44	Running	550	1 sec	335	20	1	1.0	2%
C ex 45	Electric	610	2 sec	341	16	20	35.2	44%
C ex 46	Butch	420	1 hr	342	18	2	1.0	2%
C ex 47	Running	400	1 sec	353	19	2	0.3	2%
C ex 48	Butch	300	1 hr	352	19	20	25.2	42%
C ex 49	Butch	300	30 min	347	18	1	0.4	2%
C ex 50	Running	400	1 sec	351	27	25	26.0	26%
C ex 51	Butch	290	2 hr	345	20	2	0.3	2%
C ex 52	Butch	300	30 min	342	22	20	15.0	30%
C ex 53	Electric	450	2 sec	305	25	10	3.0	10%
C ex 54	Butch	400	1 hr	291	27	10	10.0	10%
C ex 55	Running	350	1 sec	256	26	10	8.0	10%
C ex 56	Butch	500	1 hr	281	39	10	5.0	10%
C ex 57	Butch	600	1 hr	273	37	10	6.0	10%

Table 4 (cont.-7)

	Physical properties							
	Hardness at wire surface portion	Hardness at wire central portion	TS after finish cold-working	El after finish cold-working	The number of repeating times at breakage in bending	Coil life	Breakage in wire-drawing	Coil formability
	GPa	GPa	MPa	%	times			
C ex 43	1.46	1.30	403	5	6,621	○	□	×
C ex 44	1.50	1.33	342	17	2,851	×	○	○
C ex 45	1.52	1.37	384	2	7,652	○○	×	×
C ex 46	1.44	1.32	362	13	4,123	□	○	○
C ex 47	1.44	1.29	361	15	3,597	□	○	○
C ex 48	1.53	1.39	401	5	7,254	○○	×	×
C ex 49	1.41	1.30	361	17	4,102	□	○	○
C ex 50	1.42	1.30	403	3	8,654	○○	□	×
C ex 51	1.41	1.25	365	15	4,126	□	○	○
C ex 52	1.44	1.30	401	3	7,985	○○	□	×
C ex 53	1.22	1.10	319	18	2,259	×	×	○
C ex 54	1.15	1.05	301	19	3,157	×	×	○
C ex 55	1.01	0.93	282	19	2,564	×	×	○
C ex 56	1.16	1.05	304	32	2,258	×	×	○
C ex 57	1.18	1.07	308	30	2,674	×	×	○

Claims

1. A copper alloy wire, having an alloy composition containing 0.5 to 4 mass% of Ag, and at least one selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr each at a content of 0.05 to 0.3 mass%, with the balance being Cu and unavoidable impurities,
wherein the copper alloy wire has a wire diameter or a wire thickness of 0.1 mm or less, and
wherein the nanoindentation hardness in a depth region extending from the outermost surface of the wire toward at least 5% inner side in the wire diameter or the wire thickness is 1.45 GPa or more, the nanoindentation hardness at the center of the wire is less than 1.45 GPa, the tensile strength of the wire is 350 MPa or more, and the elongation of the wire is 7% or more.

2. The copper alloy wire as claimed in claim 1, wherein Ag is contained in an amount of 0.5 to 4.0 mass%.

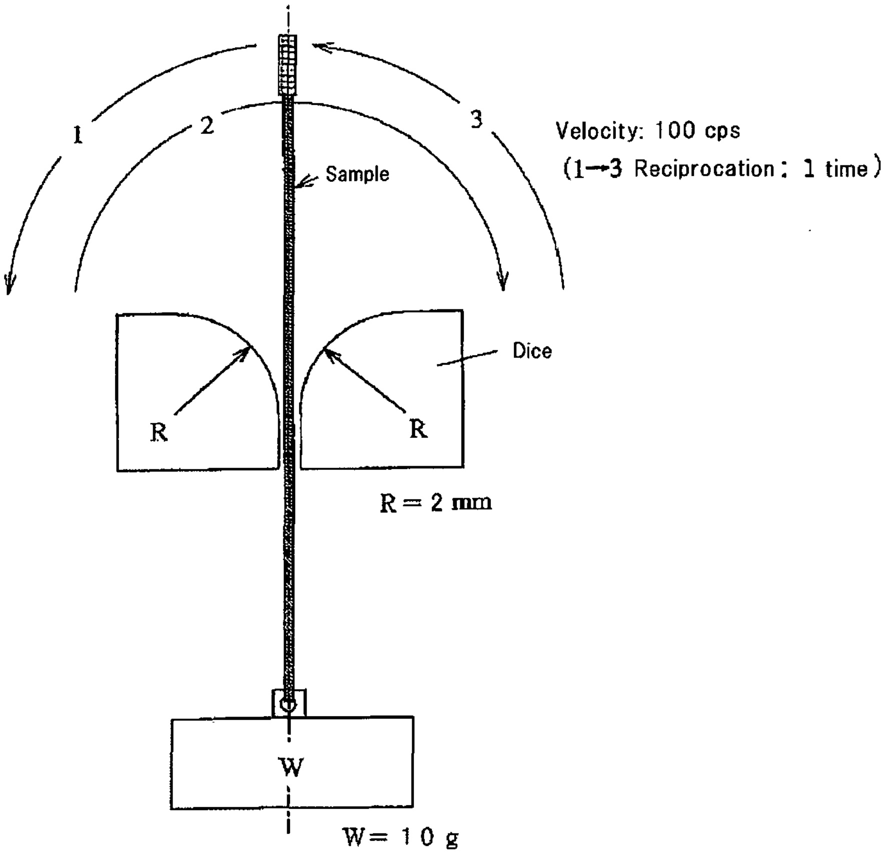
3. The copper alloy wire as claimed in claim 1, wherein at least one selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr is contained in an amount of the respective alloying element of 0.05 to 0.3 mass%.

4. A method of producing a copper alloy wire, containing the steps of:

wire-working of subjecting a rough-drawn wire of a copper alloy having an alloy composition containing 0.5 to 4 mass% of Ag, and at least one selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr each at a content of 0.05 to 0.3 mass%, with the balance being Cu and unavoidable impurities, to cold-working, to form a wire having a wire diameter or a wire thickness of 0.1 mm or less;
final-heating of subjecting the wire to heating so as to allow the wire after the heating to have a tensile strength of 330 MPa or more and an elongation of 10% or more; and
cold-working the wire that has been subjected to the heating, at a working ratio of 3 to 15%,
wherein the nanoindentation hardness in a depth region extending from the outermost surface of the wire toward at least 5% inner side in the wire diameter or the wire thickness is 1.45 GPa or more, the nanoindentation hardness at the center of the wire is less than 1.45 GPa, the tensile strength of the wire is 350 MPa or more, and the elongation of the wire is 7% or more.

5. The method of producing a copper alloy wire as claimed in claim 4,
wherein in the wire-working step, intermediate heating is carried out in the course of a plurality of cold-working steps so that the wire after this intermediate heating would have a tensile strength of 330 MPa or more and an elongation of 10% or more.

Fig. 1


1
2
3
Velocity: 100 cps
(1→3 Reciprocation: 1 time)
Sample
Dice
R
R
R = 2 mm
W
W= 1 0 g

INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2013/068160

A. CLASSIFICATION OF SUBJECT MATTER

C22C9/00(2006.01)i, *C22F1/08*(2006.01)i, *H01B1/02*(2006.01)i, *H01B5/02*(2006.01)i, *H01B13/00*(2006.01)i, *C22F1/00*(2006.01)n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C9/00, C22F1/08, H01B1/02, H01B5/02, H01B13/00, C22F1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2013
Kokai Jitsuyo Shinan Koho	1971-2013	Toroku Jitsuyo Shinan Koho	1994-2013

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2003-237428 A (Mitsubishi Cable Industries, Ltd.), 27 August 2003 (27.08.2003), entire text (Family: none)	1-5
A	JP 2008-95202 A (Fisk Alloy Wire Inc.), 24 April 2008 (24.04.2008), entire text & JP 2004-353081 A & US 2004/0238086 A1 & EP 1482063 A1 & CN 1574107 A	1-5
A	JP 2009-280860 A (Sumitomo Electric Industries, Ltd.), 03 December 2009 (03.12.2009), entire text (Family: none)	1-5

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" 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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 12 September, 2013 (12.09.13)	Date of mailing of the international search report 24 September, 2013 (24.09.13)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/068160

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2007/046378 A1 (Independent Administrative Institution National Institute for Materials Science), 26 April 2007 (26.04.2007), entire text & JP 5051647 B	1-5

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2009280860 A **[0005]**
- JP 3941304 B **[0005]**
- JP 5086445 A **[0005]**

Non-patent literature cited in the description

- *Kinzoku,* 2008, vol. 78 (9), 47 **[0019]**